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JANUARY 1959

LAMONT NATURAL RADIOCARBON MEASUREMENTS V*

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This article reports the radiocarbon age measurements made at the Lamont Geological Observatory between February 1957 and July 1958. For convenience the sample ages have been classified into the following categories:

Table	I	Geologic Samples—North American glacial geology
Table	II	Geologic Samples—Pluvial lake levels
Table	III	Geologic Samples—Relative sealevel changes
Table	IV	Geologic Samples—Oceanography
Table	V	Geologic Samples—Miscellaneous
Table	VI	Archaeologic Samples
Table	VII	Check Samples

Within each table are subdivisions according to geographic origin.

As an aid to those who do not care to scan the entire seven tables, the contents of each are summarized in the following paragraphs. Following this summary, three final items are discussed: (1) age calculations, (2) new methods of chemical pretreatment designed to detect and overcome possible sample contamination, and (3) the effect of material type on the reliability of a radiocarbon date.

Table I consists primarily of samples submitted by the Geological Survey of Canada and the United States Geological Survey. Of particular interest are the Quadra Beds in British Columbia (L-221A, B and L-424B, C, E: 25,000 to 30,000 yr), the Cook Inlet sea bluff exposure in Alaska (L-117L, L-163A, L-434: ages from 3650 to >44,000 including a finite age of 39,000) and the Port Talbot deposits on the north shore of Lake Erie (L-370A and L-440, both so old as to exceed the counter's sensitivity). For these and other sites, details are to be found in the references cited in the various sample descriptions. Other important samples are the Don interglacial beds near Toronto (L-409) and a buried soil near Richmond, Indiana (L-414), both exceeding 40,000 years in age.

Table II includes tufa samples from terraces surrounding Lake Bonneville (L-435 series) and Pyramid Lake (L-420). Shells from an elevated beach near Lake Kivu, Belgian Congo, are also listed (L-349).

* Lamont Geological Observatory Contribution No. 321.

Table III is for samples which indicate times in the past when land and sea stood at different relative positions. The new relative positions have resulted from glacial rebound, melting of glaciers, or crustal movements. Included in Table III are samples from Alaska (L-297B, E, G), Hudson Bay (L-433A, L-441A), British Columbia (L-391D, E, F; L-441B), Lower California (L-438A), Madagascar (L-403C), and Morocco (L-398A).

Table IV consists entirely of ocean sediment cores except for a carbonate sample (L-389A) dredged from the top of the Atlantis seamount. Cores are from the Cariaco Trench in the Caribbean Sea (L-430C), from the Mediterranean Sea (L-392), and from the South Atlantic Ocean off the west coast of Africa (L-421). All samples were collected by the Lamont research vessel VEMA.

Among the miscellaneous geologic samples listed in *Table V* are three buried soils from Alaska (L-400A, B, C), oölite samples from the Bahama Banks (L-418 series), and wood buried by ash ejected from the Santorin volcano on the Greek Island of Thera (L-362).

Numerous archaeologic sites are reported in *Table VI*. These include the following:

Manakaway, Conn. (L-339)	Chiapa de Corzo, Mexico (L-427)
Castle Windy, Fla. (L-377, L-405)	Chanquillo Fortress, Peru (L-404A)
Modoc Rock Shelter, Ill. (L-381C)	Grotte du Renne, France (L-399D)
Twenhafel, Ill. (L-431C)	Grotte de la Garenne, France (L-340)
Signal Butte, Nebr. (L-385)	Grotte de Taforalt, Morocco (L-399E)
Midland, Texas (L-347)	Marquesas Islands (L-394, F, J)

Kalambo Falls, N. Rhodesia (L-395B; L-399A, B, C)

Those sites with radiocarbon ages indicating the greatest antiquity of man are Kalambo Falls (>40,000), Midland (20,400), and Grotte de la Garenne (14,200).

The final table (*VII*) contains several samples measured in order to obtain interlaboratory comparisons or checks with other methods of dating—namely, historic records and the ionium-uranium age method. Samples L-292 and L-432 are checks, respectively, with the Groningen and Michigan laboratories. In both cases there is agreement within the experimental error. Additional positive interlaboratory checks have resulted as byproducts of other studies and these are reported in Table I (L-369A, L-370A, L-440, L-397C, L-397E). Besides Lamont, the other laboratories involved are Washington (U. S. Geological Survey), Yale, and Saskatchewan; all employ gas counting. Several cases in which Lamont black-carbon dates have not been substantiated by subsequent gas-counting dates are included in the Table I descriptions of samples L-117L, L-163A, and L-434.

A valuable historical check included in Table VII is sample L-371E, charred bread remains found during excavation of ash-covered Pompeii. Destruction of the city took place in A.D. 79 or about 1880 years ago. The measured C^{14} age is 1830 ± 50; it is based on 1890 oak wood as the modern control material, corrections having been made both for radioactive decay and

for the fact that 1956 Italian wheat shows a C^{13}/C^{12} isotopic ratio slightly different from the oak. Such corrections avoid the presently competing H-bomb and Suess effects which make today's organic materials unacceptable in fixing the modern control value.

Samples L-423A and L-423B in Table VII consist of calcium carbonate obtained from drill holes in Eniwetok atoll in the Pacific Ocean. Both have been dated by radiocarbon analysis and by the ionium-uranium age method (Sackett, 1958). Results are as follows:

Sample No.	Radiocarbon Age	Ionium Age
L-423A.	4900 ± 150	12,000 ± 4,000
L-423B.	23,500 ± 1000	132,000 ± 10,000

Most of the difference between the above results is probably due to younger secondary calcite cementing the original aragonitic material. Particularly is this important in sample L-423B which would require only 5.5 percent of modern calcite cement to drop its age from 132,000 to 23,500 years. Using cement-free carbonate material recently obtained, additional analyses will be made as a further check between the two dating methods.

Three final matters now to be discussed are age calculations, new methods of chemical pretreatment, and material type as it seems to affect reliability. Except where specifically mentioned in individual sample descriptions, the modern control value used to calculate ages is obtained from oak wood grown in 1890. Normalized to the same C^{13}/C^{12} ratio, this wood, after correction for 68 years of C^{14} decay, has a 3.7 ± 0.7 percent lower C^{14}/C^{12} ratio than the oxalic acid standard designated by the National Bureau of Standards. Details of the calculation methods and the gas counters used are to be found in a previous Lamont date list (Broecker, Kulp, and Tucek, 1956).

Because a radiocarbon age can be altered by the entrance of contaminating organic solutions into a sample from its environment, two chemical techniques have recently been employed in attempts to isolate a contaminant-free sample portion. These methods have been applied to wood, peat, charcoal, and burned bone and are described in detail by Olson and Broecker (1958). The first method is to employ an alkaline leach to remove so-called humic acid, the most logical contaminant in a soil environment. The second technique, limited to peat and wood, involves isolating cellulose and lignin fractions by appropriate chemical methods, the expectation being that the contaminant either will be eliminated or will follow one fraction or the other. A part of both chemical techniques is an acid leach to remove possible carbonate contamination.

At the Lamont radiocarbon laboratory, treatment for humic-acid removal is now standard practice in handling organic samples. In the course of this work, about a dozen samples have yielded sufficient humic acid for dating (in this date list, samples L-117L; L-163A; L-368; L-391B; I, L-397E; L-399C; L-400A, B, C; L-414A, B; L-424B). In only two cases—soil samples L-400A and L-400C (Table V)—has there been a significant difference between the treated sample and its humic acid, the latter being younger; hence, in the majority of cases the humic acid recovered is derived from the sample itself

and is not a contaminant. In this date list, every sample treated for humic-acid removal is so specified.

When several hundred grams of a sample are available and that sample is expected to be old, cellulose or lignin isolation is desirable. Ages of cellulose and/or lignin fractions of the following samples are reported here: L-221A, B; L-369A, B; L-370A; L-399B; and L-409. In several cases, the value of the chemical treatment is clearly demonstrated.

Inasmuch as a given percentage of modern contamination is of greatest significance in the case of old samples, contamination studies must go hand in hand with efforts to extend the radiocarbon range through C^{14} isotopic enrichment and increased counter sensitivity. Cases in point are samples L-399C (Table VI, 43,000 yr) and L-163A (Table I, 39,000 yr). These were assigned finite ages only because both were pretreated and because the humic-acid fractions of both were datable and gave ages identical to the treated sample. Even so, such old ages should be used in a conservative manner.

The question is often asked, "What materials are best for radiocarbon dating?" Certain dates reported here contribute toward an answer, providing favorable evidence for shells and both favorable and unfavorable evidence for buried soils and bone. Because shells are chemically ionic, the possibility of carbon exchange with the atmosphere or ground water must be kept in mind. That this has not occurred in sample L-391E (Table III, 12,350 yr) is evidenced by a similar age for associated wood. In addition, the 25,000-yr age on shells of sample L-438A (Table III) indicates that any exchange that may have occurred was limited; nevertheless, the age must be considered a minimum. Another sample of carbonate material showing negligible exchange is L-403C (Table III), coral limestone with an age exceeding 30,000 years.

In the case of buried soils, samples L-414A (Table I) and L-400B (Table V) demonstrate that such soils can be sealed off for thousands of years without contamination. Soil samples L-400A and C (Table V), on the other hand, show that contamination has occurred. Similarly, the bone carbonate of sample L-431C (Table VI) is consistent with archaeologic evidence, but the two burned-bone samples from Signal Butte, Nebraska (L-385C, E; Table VI) are a thousand years younger than associated charcoal.

Thus, the following conclusions seem warranted: (1) shells are gaining in stature as more dates accumulate, (2) soils and bone are less desirable but often usable, particularly if pretreated, and (3) wood and peat are superior dating materials. The third conclusion is based on the consistent humic-sample checks reported here, on the ease with which possible carbonate contaminants can be removed, on the inherent chemical variety which allows fractions to be isolated, and on the non-ionic nature of wood and peat.

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SAMPLE DESCRIPTIONS

I. GEOLOGIC SAMPLES—NORTH AMERICAN GLACIAL GEOLOGY

A. Alaska

L-117L. Nikishka No. I, Kenai Lowland, Alaska >44,000

Abraded, lignitized log in lowest 1 ft of organic lake silt section, 8 ft thick, overlying iron-stained and contorted gravel exposed near base of Cook Inlet sea bluffs (60° 51′ N Lat, 151° 24′ W Long), 2.5 mi S of Naptowne end moraine at East Foreland, Alaska. The log is transported and could have been either derived from vegetation growing at the time of initial lake deposition or reworked from the subjacent older gravel unit of pre-Naptowne age. The antiquity and lignitized character of the sample suggest derivation from the underlying gravel. The geology of the area is described in a U. S. Geological Survey report now in preparation (T. N. V. Karlstrom, personal communication). Sample L-117L is part of a group of Cook Inlet C^{14} samples, including material collected from directly beneath Naptowne till, which were dated by the black-carbon method between 14,000 and 22,000 B.P. and suggested a late-Wisconsin age for the Naptowne glaciation (Karlstrom, 1952, and *in* Péwé and others, 1953). All these samples have been rerun by the more accurate gas-counting methods. All gave ages of >32,000 B.P., indicating that the early black-carbon results in this finite older age range were spuriously young, and requiring a revision in the correlation of the Naptowne glaciation of Cook Inlet with all, not just part, of the type Wisconsin deposits (Karlstrom, 1955, 1957). Coll. 1951 and subm. by T. N. V. Karlstrom, U. S. Geological Survey. *Comment*: sample L-117L was previously dated by the black-carbon method at 19,200 ± 1000 yr as reported by Kulp and others (1952). The sample reported here was treated for humic-acid removal.

L-117L. Residue after humic-acid removal **>44,000**
L-117L. Humic acid **>40,000**

Other related Cook Inlet samples dated by the black-carbon method include samples L-101B (14,300 ± 600) and L-117J (15,800 ± 400) as reported by Kulp and others (1951); L-117A (19,100 ± 900) as reported by Kulp and others (1952); and L-163A (22,000 ± 2000, previously unpublished black-carbon result). Reruns by the gas-counting methods of samples L-101B,[1] L-117A, L-117J, and L-163A gave ages respectively of >38,000 (W-535; Robert Miller, U. S. Geological Survey, personal communication), >32,000 (W-76; Suess, 1954), >32,000 (W-77; Suess, 1954), and 39,000 ± 2000 (L-163A; this paper).

L-163A. Salamato Beach, Kenai Lowland, Alaska 39,000 ± 2000

Iron-stained lignitized log collected from silt, sand, and gravel unit conformably overlain by coarse gravel, and unconformably overlying contorted gravel and silt unit as exposed in upper part of Cook Inlet sea bluffs (60° 40′ N Lat, 151° 23′ W Long) about 3.5 mi S of the Naptowne end moraine at East Foreland, Alaska. The sampled intermediate stratigraphic unit is traceable northward in the sea bluffs up to and beneath Naptowne till at East Foreland (Wisconsin till according to Karlstrom) and apparently represents in large part lacustrine and fluvial sedimentation during the advancing phases of an ice

tongue from Alaska Range sources, across Cook Inlet into the vicinity of East Foreland during Naptowne time (Karlstrom, report in preparation). This sample is the first from Alaska to be finitely dated in this age range. Its stratigraphic position and apparent age give promise that the interval preceding the last major glaciation in Cook Inlet, Alaska may be datable in the extending 40,000 to 60,000-yr C^{14} range. Coll. 1951 and subm. by T. N. V. Karlstrom. *Comment*: sample L-137D (Broecker and others, 1956), collected near Kenai from a comparable stratigraphic position in the sea bluffs but closer to beach level, was dated by the black-carbon method at >24,000. Sample 163A itself was previously dated by the black-carbon method and gave an age of 22,000 ± 2000. The age reported here is based on two portions of the original sample: the residue after humic-acid removal and the humic acid itself. Of six measurements, only two differed from average background by less than four times the standard error of the background; and these two exceeded the background by twice its standard error.

L-163A. Residue after humic-acid removal **39,000 ± 2600**
L-163A. Humic acid **39,000 ± 2000**

L-434. Third Bay, Kenai Lowland, Alaska **3700 ± 150**

Wood from beaver-gnawed debris in a beaver-house pocket immediately beneath a 5 to 9-ft peat unit in a surface bog deposit exposed in Cook Inlet sea bluffs of Third Bay (60° 47′ N Lat, 151° 12′ W Long) within 1 mi. and E. of the Naptowne end moraine at Boulder Point, Alaska. The geology of the area and stratigraphy of the coastal bogs are described in a U. S. Geological Survey report now in preparation (T. N. V. Karlstrom, personal communication). Coll. 1950 and subm. by T. N. V. Karlstrom. *Comment*: this sample was treated for humic-acid removal. Under the number L-163C a portion of this sample was dated by the black-carbon method as 3100 ± 400. Related samples include L-117N (Kulp and others, 1952; 3800 ± 400) of spruce wood collected from the basal peat 1 ft above sample L-434; and L-163E and F (3550 ± 170 and 3950 ± 200; previously unpublished black-carbon results) of spruce and birch wood collected respectively 6 in. above and from along the contact of the same stratigraphic horizon in another coastal bog 6 mi E of the L-434 and L-117N-collecting locality. Results from these four samples, within statistics, are consistent with each other and with stratigraphic position.

Samples **L-163B** and **L-1170 (8650 ± 450** and **8200 ± 900;** previously unpublished black-carbon results) are wood and organic silt near the base of a lower 4-ft peat bed overlain by organic silt in the same bog and collected by Karlstrom about 9 ft below sample L-434. These results compare with wood and organic-silt samples L-137D and L-163D (9500 ± 600 and 9200 ± 600; Broecker and others, 1956) and wood samples W-602 and W-603 (8470 ± 300 and 8950 ± 280; Karlstrom, U. S. Geological Survey personal communication). Coll. by Karlstrom just beneath and along comparable stratigraphic horizons exposed in three bogs in the Turnagain Arm sea bluffs near Point Possession 40 mi NE of Boulder Point.

L-301. Kogosukruk River, Alaska **>36,000**

Larch wood from a bank in a cut of the Kogosukruk River (69° 45′ N Lat, 151° 40′ W Long), Alaska. Sample came from a gravelly layer in the zone

of contact between the unconsolidated Gubik Formation and the Cretaceous Colville Formation. Probably of marine origin at this site, the Gubik is thought to be Pleistocene in age. Coll. 1953 by J. C. F. Tedrow; subm. by Boston University Physical Research Laboratory. *Comment*: sample was first given a finite age of 24,000 ± 2000. Since the geologic evidence suggested an age beyond the range of the Lamont counters, a new sample portion was measured; the above age of >36,000 was then obtained. Whether field or laboratory contamination caused the finite age has not been determined.

L-368. Nelchina River, Alaska **8450 ± 200**

Peat with high silt content from north bank of Nelchina River (61° 57′ N Lat, 146° 57′ W Long) 3 mi S of milepost 137, Glenn Highway, southwestern Copper River Basin, Alaska. Buried 8 ft below the surface, the sample provides a minimum date for (1) contorted gravel at base of the section, deposited as Nelchina Glacier retreated (its terminus now lies 14 mi S) and (2) stratified lacustrine sand and silt above the contorted gravel but below the dated material. Geologic report is in preparation. Coll. 1954 and subm. by J. R. Williams, U. S. Geological Survey. *Comment*: this sample was treated for humic-acid removal and enough humic acid was recovered for dating.

L-368.	Residue after humic-acid removal	**7550 ± 500**
L-368.	Humic acid	**8450 ± 200**

The humic-acid age is preferred because the amount of CO_2 recovered from the treated residue was quite small, requiring dilution with CO_2 from anthracite coal. A peat sample (L-237B, unpublished) collected by Williams in 1952 from the same section as L-368 but 16 ft below gave an anomalously young age which has not yet been explained. Three separate measurements were made:

L-237B.	Untreated (black-carbon method)	**600 ± 240**
L-237B.	Untreated (CO_2 method)	**950 ± 200**
L-237B.	Residue after humic-acid removal (CO_2)	**900 ± 300**

L-297A. Lemon Creek Glacier, Alaska **10,300 ± 600**

Basal ligneous peat from a depth of 18 ft in muskeg (58° 23′ 30″ N Lat, 134° 25′ 20″ W Long) 6 mi N of Juneau, Alaska. Sample was obtained at a 750-ft elevation, about 1000 ft from the position attained around A.D. 1750 by the lower tongue of Lemon Creek Glacier. The sample age is the earliest postglacial date thus far obtained in this district and indicates that the 1750 glacier position has not been exceeded for at least the past 10,000 years. Coll. 1955 and subm. by C. L. Heusser, American Geographical Society. *Comment*: the same age was obtained for basal sedge peat collected several miles away (L-297D; Broecker and Kulp, 1957).

B. Canada

L-391I. Avalon Peninsula, Newfoundland **7400 ± 150**

Basal peat from a bog (47° 29′ N Lat, 52° 46′ W Long), 17 ft thick, on Avalon Peninsula, Newfoundland. Sample gives a minimum age for deglaciation of the St. John's, Newfoundland area. Coll. 1956 by E. P. Henderson; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal and enough material was recovered for dating.

L-391I.	Residue after humic-acid removal	**7400 ± 150**
L-391I.	Humic acid	**7350 ± 300**

L-369A. St. Pierre les Becquets, Quebec >44,000

Wood from a peat bed exposed in a stream bank, 90 ft high, near St. Pierre les Becquets (46° 29′ N Lat, 72° 12′ W Long), Nicolet County, Quebec. The geology of the area is described by Gadd (1955). Coll. 1954 by N. R. Gadd; subm. by Geological Survey of Canada. *Comment*: this sample has been dated by three laboratories in the past (Rubin and Suess, 1955, W-189; Preston and others, 1955, Y-242; Broecker and Kulp, 1957, L-190A); all ages have exceeded counting range. The age reported here is for lignin isolated from wood.

L-369B. Missinaibi, Ontario >42,600

Wood from between two till sequences exposed in a bank cut by the Missinaibi River (50° 19′ N Lat, 82° 42′ W Long) about 6 mi upstream from its confluence with the Soweska River, 125 mi SW of James Bay, Ontario. Sample is from base of non-glacial beds, 17 ft thick, containing wood, peat, and organic silt and sand. The wood was separated from the remainder of the non-glacial sequence by a lens of till-like material, 3 ft thick, probably colluvium. The non-glacial beds overlie a complex of till and gravel and are overlain in turn by till. Sample probably dates a non-glacial interval with climate there much like that today. The geology of the area is described by McLearn (1926). Coll. 1954 by O. L. Hughes; subm. by Geological Survey of Canada. *Comment*: the above age supersedes the four finite ages (37,700 to 38,900) reported by Olson and Broecker (1957) for cellulose and lignin fractions of the wood and the peat above it. The age reported here is for a re-count of the wood cellulose. Untreated wood yielded an age of >40,500.

L-391A. Coulson Township, Ontario 3450 ± 300

Fresh peat from a depth of 8.65 to 8.80 ft at the base of a bog impounded behind a Lake-Barlow-Ojibway bay-mouth bar located in Coulson Township (48° 38′ N Lat, 80° 21′ W Long), Northern Ontario. Sample indicates the minimum age for the bay-mouth bar. Coll. 1956 by O. L. Hughes; subm. by Geological Survey of Canada.

L-391B. Cochrane, Ontario 4750 ± 250

Peat from a depth of 386 cm at the base of a bog (49° 2′ N Lat, 80° 59′ W Long) resting on gray silty clay 1.5 mi SE of Cochrane, Ontario, on the Ontario Northland Railway. Sample age indicates the beginning of peat formation following the close of the Lake Barlow-Ojibway episode. Coll. 1956 by J. Terasmae; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal and enough humic acid was recovered for dating.

L-391B.	Residue after humic-acid removal	**4750 ± 250**
L-391B.	Humic acid	**4650 ± 180**

L-433C. Cochrane, Ontario 5300 ± 120

Peat from a bog exposed on the south side of Highway 11 near Cochrane (49° 3′ N Lat, 81° 6′ W Long), Ontario, about 1.65 mi E of bridge over Frederick House River. Sample comes from the lowest 1 in. of the bog profile. Sample age indicates the time of earliest peat formation following the Lake

Barlow-Ojibway episode. Coll. 1957 by J. Terasmae; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal.

L-409. Don Valley, Ontario **>46,000**

Wood from an exposure of the Don Beds in the Don Valley Brick Yards near Toronto, Ontario (43° 41′ N Lat, 79° 22′ W Long). Sample was found 3 to 4 ft above the contact with the Dundas Ordovician shale and limestone. Sandwiched between two distinct tills above and one below, the Don sands contain warm-climate fossils. Watt (1954) judged the Don beds to be of Sangamon age; thus the age of the enclosed wood should exceed the range of the Lamont counters. Coll. 1957 and subm. by A. K. Watt, Ontario Water Resources Commission. *Comment*: cellulose and lignin fractions were isolated. Without such isolation, a finite age would have been given for the sample. The appearance of the younger contaminant in the cellulose rather than in the lignin is inconsistent with the postulate that the contaminant is humic acid.

L-409.	Wood lignin	**>46,000**
L-409.	Wood cellulose	**40,200 ± 1600**
L-409.	Untreated wood	**43,100 ± 3000**

L-370A. Port Talbot, Ontario **>40,000**

Gytta from lens in silt exposed on the shore of Lake Erie, abount 0.5 mi SW of Port Talbot, Ontario (42° 38′ N Lat, 81° 23′ W Long). Beneath the silt are varved clay and sandy till; above it are several tills and lacustrine deposits. Glacial geology is described by Dreimanis (1957, 1958) who considers the gyttja to have formed shortly after the Early Wisconsin sub-age. Coll. 1956 and subm. by A. Dreimanis and W. S. Broecker. *Comment*: other radiocarbon dates for the area are summarized by Dreimanis (1957); among them are ages of four samples correlative with L-370A, all of which exceed the radiocarbon-counting range of the three laboratories reporting the ages. In addition, L-440 (this date list) is the age of wood from the till above this sample. Gyttja sample reported here was measured in two ways:

L-370A.	Untreated	**33,000 ± 1500**
L-370A.	Cellulose	**>40,000**

L-440. Port Talbot, Ontario **>29,500**

Coniferous wood from gravelly till (no. 2 of Dreimanis, 1957) in the shore cliff of Lake Erie (42° 38′ N Lat, 81° 23′ W Long). Found with a mastodon tusk and beneath two other tills, the wood may indicate a glacial advance breaking up the big interstadial period between Early Wisconsin glacial time and the 25,000-year-old main Wisconsin glacial time. The geology of this area, with other radiocarbon dates and definitions of chronologic terms, is discussed by Dreimanis (1957, 1958). Coll. 1957 and subm. by A. Dreimanis, University of Western Ontario. *Comment*: this sample was a 13-gram piece of wood whittled clean of slightly moldy outside material. It was treated for humic-acid removal. There is a distinct possibility that the sample has a finite age. Five 1000-min counts were made, one of which was 0.1 cpm below background, each of the other four exceeding background by at least 0.4 cpm. If the single low count were excluded, the sample age would be 33,000 ± 3000. Even including the low count, the average net sample count equals twice its

error. Because the same wood has been dated by the University of Saskatchewan as >34,000 (S-46; Dreimanis, 1958), it seems wise not to quote a finite age until a larger sample becomes available for further measurement. Below this sample in the stratigraphic column is L-370A (this date list) with an age exceeding 40,000; above it in the next-younger till are L-185B (28,200 ± 1500) and L-217B (24,000 ± 1600) (Broecker and Kulp, 1957).

L-391H. High River, Alberta **4200 ± 150**

Wood from 1 ft above the base of a 15-ft section (50° 35′ N Lat, 113° 52′ W Long) of floodplain silt overlying gravel near High River, Alberta, in the abandoned valley of Little Bow River. Sample age indicates the minimum time elapsed since diversion of Highwood River from Little Bow Valley to its present course northward from High River. Coll. 1955 by A. M. Stalker; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal.

Quadra Beds, British Columbia

In the Vancouver Island area, Quadra marine and fluvial beds unconformably underlie Vashon glacial sediments, the latter having been deposited during a single major Wisconsin glaciation. From field evidence alone it appeared that Quadra carbonaceous materials should have ages exceeding 40,000 years. However, the samples listed below indicate deposition 25,000 to 30,000 yr B.P. Geology is discussed in detail by Fyles (1956).

L-221. Dashwood Cliff, Vancouver Island, British Columbia

Wood and peat from the base of the Quadra sediments exposed at Dashwood (49° 22′ N Lat, 124° 31′ W Long) near Qualicum Beach on Vancouver Island, British Columbia. Both samples were from a peat bed, 40 in. thick, in sediments thought to correlate with similar deposits throughout the Georgia Basin. Coll. 1953 by J. G. Fyles; subm. by Geological Survey of Canada. *Comment*: both peat and wood were previously dated by the black-carbon method (Broecker and others, 1956) as >24,000 and >26,000 respectively. The dates reported here are for chemical fractions isolated according to techniques described by Olson and Broecker (1958).

L-221A.	Wood cellulose	**25,900 ± 300**
L-221A.	Wood lignin	**25,850 ± 500**
L-221B.	Peat cellulose	**23,450 ± 300**
L-221B.	Peat lignin	**25,050 ± 300**

L-424B. Denman Island, British Columbia **30,200 ± 1300**

Peat exposed in the lower part of the Quadra sediments in the northwestern part of Komas Bluff (49° 36′ N Lat, 124° 49′ W Long), Denman Island, British Columbia. Coll. 1957 by J. G. Fyles; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal and sufficient humic acid was obtained for dating.

L-424B.	Residue after humic-acid removal	**30,200 ± 1300**
L-424B.	Humic acid	**32,300 ± 1800**

L-424C. Denman Island, British Columbia **29,300 ± 1400**

Wood from a sand lens in Komas Bluff (49 36′ N Lat, 124° 49′ W Long), Denman Island, British Columbia. Lens forms part of the silt-gravel-

peat unit located in lower Quadra sediments. Coll. 1957 by J. G. Fyles; subm. by Geological Survey of Canada.

L-424E. Denman Island, British Columbia 30,000 ± 1[illegible]0

Wood from the silt-gravel-peat unit of the Quadra sediments, Komas [illegible] (49° 36′ N Lat, 124° 49′ W Long), Denman Island, British Columbia. Coll. 1957 by J. G. Fyles; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal.

L-428. Thelon River, Northwest Territories 5500 ± 250

Leaves of *Ceratophyllum demersum* collected 3 ft below the surface in a gullied pingo (64° 19′ N Lat, 102° 41′ W Long), adjacent to the Thelon River, Northwest Territories, Canada. Numerous laminae of the plant material are encased in the silt, which probably accumulated in a small pond or on a floodplain. Age of the sample sets a lower limit on the duration of postglacial time in this region. Coll. 1955 by B. G. Craig; subm. by Geological Survey of Canada.

L-300A. Mackenzie Delta, Northwest Territories >33,000

Driftwood from a pingo, 130 ft high (69° 27′ N Lat, 133° 04′ W Long), in the Mackenzie Delta, Northwest Territories, Canada. Sample was found below deposits of apparently glacial origin; these in turn were overlain by lake deposits containing mollusk shells. It was hoped that the sample age would provide better evidence concerning the maximum period for postglacial pingo formation, a period known to be less than the several thousand years since glacial retreat in the area, but the age is too great to be of value. Müller (in press) describes the pingos of the region. Coll. 1955 and subm. by F. Müller. *Comment*: another sample of driftwood from the same pingo and from the same stratigraphic section (10 ft higher but still below the glacial deposits) was dated by Dr. Oeschger, University of Berne, Switzerland, at 28,000 ± 2000 years (F. Müller, personal communication.)

C. United States

L-380. Worcester, Massachusetts >30,000

Peat from a road cut (42° 12′ N Lat, 71° 47′ W Long) exposed during construction of the Massachusetts Turnpike near Worcester. Having almost the consistency of lignite, the peat comprises a layer, 1 to 2 ft thick, interbedded between underlying shallow-lake sediments and about 65 ft of till above. No other till exists above the regional Paleozoic bedrock. Coll. 1956 and subm. by E. S. Barghoorn, Harvard University. He (personal communication) believes the till represents the last ice advance in the area. From his study of the peat microfossils, he concludes that the flora closely resembles that in Eastern Massachusetts today, representing possibly a slightly warmer climate. On this basis, he judges the peat to be interglacial. *Comment*: sample was treated for humic-acid removal.

L-397C. Dayton, Ohio 20,000 ± 500

Wood from within the Camden moraine (39° 39′ N Lat, 84° 11′ W Long), 6 mi S of Dayton, Montgomery County, Ohio. Sample was entirely en-

cased in till and lay beneath 19 ft Cary till and sand. Coll. 1947 and subm. by R. P. Goldthwait, Ohio State University. *Comment*: sample was dated previously by Suess (1954, W-37) and gave an age of 20,700 ± 600. Lamont secured an additional portion for humic-acid removal and the treated sample age is that above. The check between the two laboratories indicates absence of humic-acid contamination in the original sample.

L-397E. Germantown, Ohio **>44,000**

Wood from a cut of the Twin Creek River (39° 37′ N Lat, 84° 21′ W Long) near Germantown, Montgomery County, Ohio. Sample came from a peat layer, 8 ft thick, overlying till and itself overlain by 60 ft of calcareous till. According to Goldthwait (1958), the peat layer antedates the upper till by a considerable time. Coll. by E. Orton; subm. by R. P. Goldthwait. *Comment*: sample was dated previously by Suess (1954, W-96) and gave an age of >34,000. Lamont secured an additional portion for humic-acid removal. The age given above was obtained on the humic acid extracted because the sample residue was too small for dating.

L-414. Darrah Farm, Indiana **>41,000**

Humus-rich humic-gley soil with included wood from the Darrah Farm (39° 47′ N Lat, 84° 59′ W Long) 5 mi SW of Richmond, Indiana. This buried soil, about 23 in. thick, is overlain by 28 in. of leached sand covered by calcareous till considered by both Gamble (1958) and by J. Thorp and A. Gooding (personal communication) to be of early Wisconsin age. Numerous buried soils in the area seem to correlate with the Darrah Farm soil but have not been C^{14}-dated as yet. Coll. 1957 by E. Gamble and A. Gooding; subm. by J. Thorp, Earlham College. *Comment*: both the soil and the included wood were treated for humic-acid removal. In each case enough humic acid was recovered for dating.

L-414A.	Soil residue after humic-acid removal	**>34,000**
L-414A.	Soil humic acid	**>41,000**
L-414B.	Wood residue after humic-acid removal	**>29,000**
L-414B.	Wood humic acid	**>33,000**

This site was previously dated by Broecker and others (1956) at 30,000 ± 8000, using calcium carbonate prepared from soil organic by the U. S. Dept. of Agriculture, Beltsville, Maryland Station.

II. GEOLOGIC SAMPLES—PLUVIAL LAKE LEVELS

A. North America

L-420. Pyramid Lake, Nevada **19,100 ± 700**

Crystals of thinolite tufa collected on the western shoreline of Pyramid Lake (39° 58′ N Lat, 119° 38′ W Long) about 3 mi N of Sutcliffe, Nevada. Samples were taken from the surface of an exposed mud flat about 3 ft from the water's edge; the crystals were oriented perpendicular to the surface. See Radbruch (1957) for a discussion of the origin of thinolite tufa. Coll. 1957 and subm. by D. H. Radbruch, U. S. Geological Survey. *Comment*: the age of this sample was calculated using the C^{14}/C^{12} ratio in dissolved bicarbonate from Pyramid Lake (Broecker and Walton, in press).

L-435. Provo Terrace, Utah

Tufa samples collected from Provo Terrace (alt. 4880 ft) at the north end of the Oquirrh Mountain Range (40° 42′ N Lat, 112° 20′ W Long) opposite Great Salt Lake. Presumably tufa was formed during high-water phases of Lake Bonneville. See Broecker and Orr (1958) for a radiocarbon chronology of Lakes Lahontan and Bonneville based in part on tufa samples. Coll. 1957 and subm. by W. S. Broecker and A. Walton, Columbia University. *Comment*: all samples were pre-treated with acid to remove a thin outer layer. The problem of tufa contamination by postdepositional exchange with atmospheric and water-dissolved CO_2 is discussed by Broecker and Orr (1958). Although they conclude that atmospheric contamination is not likely to occur to a significant degree, only limited data are presented for the case of exchange with water-dissolved CO_2. The modern control value recommended by them has been used in calculating the age of the L-435 series.

L-435D. Provo Terrace, Utah **14,800 ± 600**

Massive tufa directly overlying the bedrock into which the terrace was cut. The 4-in. tufa horizon from which the sample was taken is covered by a more recent layer of similar tufa.

L-435K. Provo Terrace, Utah **16,400 ± 400**

Tufa cementing gravel into which the Provo terrace was cut. This gravel is overlain by a layer of pure tufa with a radiocarbon age of 15,530 ± 280 yr (Broecker and Kulp, 1957; L-363E).

L-435G. Provo Terrace, Utah **11,300 ± 250**

Tufa cementing gravels that form part of the terrace.

L-435F. Provo Terrace, Utah **9150 ± 200**

Relatively pure tufa from beneath the gravels from which sample L-435G was taken. The material leached from this sample yielded an age of 8500 ± 200. The age is anomalously young, suggesting that it was contaminated by recent leaching of the gravels.

L-435C. Provo Terrace, Utah **10,600 ± 300**

Tufa from a 6-in. layer covering a portion of the Provo Terrace. The material leached from the surface of this sample yielded an age of 9050 ± 200 yr.

L-435B. Provo Terrace, Utah **13,100 ± 250**

Tufa cementing coarse gravel into which the terrace was cut.

B. Africa

L-349A. Lake Kivu, East Africa **12,450 ± 350**

Shells from a terrace 330 ft (100 m) above the level of Lake Kivu at Kisenyi (1° 42′ S Lat, 29° 16′ E Long), Ruanda. Sample was imbedded in a sandy-clay bed interstratified with coarse sand and volcanic ash at the former mouth of the Sebeya stream. Apparently the shells date a high level of the lake. Coll. 1955 by A. Meyer; subm. by the Director of Geological Survey of Belgian Congo. *Comment*: the age of the shells was calculated assuming that the C^{14}/C^{12} ratio in the lake is equal to that in the atmosphere. Sample L-349B (reported in this date list) was originally submitted as a control sample but ap-

pears to be fossil rather than recent. Since the C^{14}/C^{12} ratio in the lake may have been less than that assumed for the age calculated, the age should be considered a maximum.

L-349B. Lake Kivu, East Africa **14,000 ± 600**

Lamellibranch shells from Kirotshe beach, Belgian Congo (1° 36′ S Lat, 29° 02′ E Long) at the northwest corner of Lake Kivu. Originally, it was thought that the shells should be modern, but the old radiocarbon age is consistent with two facts pointing to the shells being ancient: (1) no living lamellibranch mollusks have been found in the vicinity, and (2) excavated pits in the area show a nearly continuous buried shell layer. Thus the shell age probably dates a former level of the lake close to the present level. Lake Kivu must have passed the present level before reaching the high level dated by sample L-349A. Coll. 1955 by A. Meyer; subm. by the Director of Geological Survey of Belgian Congo. *Comment*: the age is based on an initial C^{14}/C^{12} ratio equal to that in atmospheric CO_2 and hence must be considered maximum.

III. GEOLOGIC SAMPLES—RELATIVE SEALEVEL CHANGES

A. North America

L-189B. Coquille, Oregon **350 ± 150**

Charcoal buried under 7 ft of floodplain silt deposited by the meandering Coquille River about 1 mi S of Coquille, Oregon (43° 10′ N Lat, 124° 11′ W Long). Charcoal is associated with mussel shells, fireplaces, and artifacts. Since sample lies at a sharp sand-silt boundary, its age provides chronologic information as to the time when the velocity of the Coquille River decreased, perhaps owing to relative rise of sealevel. Coll. 1952 and subm. by L. S. Cressman, University of Oregon. *Comment*: because of the unexpectedly young sample age, additional charcoal (L-388A) from the same site was dated following treatment for humic-acid removal, and essentially the same age was obtained.

L-297G,E,B. Juneau, Alaska

This is a sequence of basal peats from muskegs situated at various elevations below the limit of late-glacial and early postglacial marine transgression. As a result of glacial rebound, this limit in the Juneau district is now elevated to as much as 500 ft above present sealevel. Since the sampling area has an annual rainfall of about 100 in., peat should begin forming almost immediately after emergence. On this basis the ages of basal peats at higher elevations should exceed those at lower elevations. The ages of the following samples show this to be so. Further support comes from the fact that pollen profiles at the 40-ft and 10-ft elevations (samples L-297E and B respectively) lack a basal section present in the profile at 150 ft (L-297G); this points to peat forming at higher elevations while the lower areas were inundated. Hence, this sequence of radiocarbon dates provides a chronology of both emergence and uplift. Samples coll. and subm. by C. J. Heusser, American Geographical Society.

L-297G. Montana Creek Road **7800 ± 300**

Ligneous peat from a 19.5-ft depth at site along Montana Creek Road 11 mi NW of Juneau, Alaska, elevation about 150 ft (58° 25′ 20″ N Lat, 134°

36′ 40″ W Long). The pollen record indicates the sample age to be early Hypsithermal (see Deevey and Flint, 1957). Till with marine fossils is present in the Upper Montana Creek valley at elevations up to 400 ft, showing that the sample site was once beneath the sea (Twenhofel, 1952). *Comment*: sample L-297D (Broecker and Kulp, 1957) is of basal sedge peat (elevation 750 ft) from another locality along the Montana Creek Road about 8 mi from L-297G. Since the pollen of L-297D is early pine, its age of 10,300 ± 400 gives an approximate date to the recession of the last area glacier. If this date is taken as the time when glacial rebound began, the average rate of emergence between elevations 400 ft and 150 ft was about 10 ft per century.

L-297E. Glacier Highway **6650 ± 250**

Sedge peat at a 9.6-ft depth near milepost 11.5 along Glacier Highway NW of Juneau, Alaska, elevation about 40 ft (58° 22′ 30″ N Lat, 134° 36′ 40″ W Long). The sample age, together with the content and stratigraphy of pollen in the overlying section, indicates that muskeg formation began during the Hypsithermal interval. *Comment*: based on the ages of this sample and L-297G above, average rate of emergence between 150-ft and 40-ft positions approximates 10 ft per century.

L-297B. Sunny Point **6100 ± 300**

Sedge peat from a 15.8-ft depth on Gastineau Channel at milepost 7.5 along Glacier Highway northwest of Juneau, Alaska, elevation about 10 ft (58° 21′ 35″ N Lat, 134° 31′ 40″ W Long). The sample age is also Hypsithermal. In combination with pollen content and stratigraphy of the overlying peat, the sample age indicates that sealevel has not risen above the present 10-ft elevation within the last 6100 years. *Comment*: based on the ages of this sample and L-297E above, average rate of emergence from elevation 40 ft to 10 ft approximates 5 ft per century. Within the last 6100 years, the rate has dropped to almost nothing, averaging about 2 in. per century.

L-391D, E. Parksville, Vancouver Island

Wood and shells from the bottomset sand and clay of a delta of the Englishman River near Parksville (49° 17′ N Lat, 124° 02′ W Long) on the east-central coast of Vancouver Island, Canada. The delta, thought to mark a marine stand, is now 170 ft above sealevel. Coll. 1956 by J. G. Fyles; subm. by Geological Survey of Canada.

L-391D. Wood **12,150 ± 250**
L-391E. Marine shells **12,350 ± 250**

Comment: the agreement between these two dates is evidence for the reliability of dates on marine shell.

L-391F. Fanny Bay, Vancouver Island **11,850 ± 300**

Wood from bottomset sand of a delta of Wilfred Creek at Fanny Bay (49° 29′ N Lat, 125° 49′ W Long) near Courtenay on the east-central coast of Vancouver Island. The delta, thought to mark a marine stand, is now 70 ft above sealevel. Coll. 1956 by J. G. Fyles; subm. by Geological Survey of Canada.

L-433A. Fort George, Quebec **3700 ± 130**

Wood from the bank of the Fort George River 36 mi E of Fort George (58° 44′ N Lat, 78° 11′ W Long), Quebec. Associated with marine shells, the

wood lay beneath 15 ft of surface sands and 40 ft of stony clay. Since the top of the stony silt is now 175 ft above sealevel, this sample dates an ancient sea stand and indicates the magnitude of glacial rebound. Coll. 1957 by H. A. Lee; subm. by Geological Survey of Canada. *Comment*: sample was treated for humic-acid removal.

L-438A. El Pulmo, Mexico **25,400 ± 1000**

Shells of *Glycymeris maculata* taken from fossiliferous beds approximately 12 ft above sealevel at El Pulmo (23° 26′ N Lat, 109° 25′ W Long), Baja California, Mexico. Beds are thought to be of late Pleistocene age and to have been uplifted rather than deposited during a higher stand of sealevel. The basal portion of this sequence represents the foundation rock for the coral reef at El Pulmo reported by Ricketts *in* Steinbeck and Ricketts (1941). Coll. 1957 and subm. by D. F. Squires, American Museum of Natural History. *Comment*: shells were preleached with acid in order to remove possible contamination. Since there is no assurance that more recent carbonate was completely removed, the age must be considered a minimum.

L-441A. Great Whale River, Quebec **3020 ± 120**

Wood from terrace, elevation 20 ft, at settlement of Great Whale River (55° 16′ N Lat, 77° 43′ W Long), Quebec (Hudson Bay). The wood came from silt containing marine shells 6.5 ft beneath the surface of a terrace cut into the marine deposits by the river. The marine deposits enclosing the wood probably correlate with the 90-ft strandline found throughout the area. Coll. 1957 by H. A. Lee; subm. by Geological Survey of Canada.

L-441B. Denman Island, British Columbia **11,500 ± 200**

Marine shells from Komas Bluff (49° 35′ N Lat, 124° 49′ W Long), Denman Island, British Columbia (Strait of Georgia). The shells were collected from a postglacial beach 120 ft above sealevel. Coll. 1956 by J. G. Fyles; subm. by Geological Survey of Canada. *Comment*: samples L-391D, E, and F (reported in this date list) represent similar shoreline positions in the same region.

B. Africa

L-398A. Rabat, Morocco **800 ± 200**

Charcoal fragments imbedded in an alluvial terrace of the Bou Regreg Valley (34° 02′ N Lat, 6° 50′ W Long) near Rabat, Morocco. Sample was associated with Neolithic (or younger) pottery debris about 9 ft below the surface of the lowest alluvial terrace. The alluvium of that terrace unconformably overlies estuarine clay which is associated with fine-grained littoral shell sands and is believed to be of Flandrian age (Gigout, 1954). The date confirms that the last alluviation was post-Altithermal (3500 to 7500 B.P.), and, because the terrace is 7 ft above present mean sealevel, it points to a late Recent stage of high sealevel and/or high rainfall in Morocco. Mean sealevel 1000 yr B.P. was probably 3 ft above the present (see "Rottnest" terrace of Fairbridge, 1958), but contemporary fluvial deposits could, of course, build up higher Coll. 1956 by M. Gigout; subm. by R. W. Fairbridge, Columbia University.

L-403C. Ambanja, Madagascar **>30,000**

Coral limestone from a buried coral reef near Ambanja (13° 39′ S Lat, 48° 26′ E Long), Madagascar. The coral (madreporarian) grew in situ when

sealevel stood somewhat below its present level. Specimen came from a well sunk in the innermost part of the Sambirano delta, from a depth of 55 to 60 ft beneath the delta plain, and about 5 to 10 ft below mean sealevel. A dating in the postglacial range would have indicated the mean rate of delta growth and also the time of a former sealevel in this rather stable region. Coll. 1957 by R. Battistini; subm. by R. W. Fairbridge.

IV. GEOLOGIC SAMPLES—OCEANOGRAPHY

A. Atlantic Ocean

L-421. Walvis Shelf, South Atlantic Ocean

Organic material from a diatomite layer in a core (V-12-64) taken in the South Atlantic Ocean off the west coast of Africa (22° 34′ 12″ S Lat, 14° 12′ 00″ E Long) along the continental shelf. The diatomite layer is underlain by a mixture of sand and coarse shell fragments. Coll. 1956 and subm. by R. Menzies, Columbia University. *Comment*: sample ages are computed using the C^{14}/C^{12} ratio measured for plankton that was collected in the same area in 1957. The Plankton has a C^{14}/C^{12} ratio 7.8% below that in age-corrected 1890 wood.

L-421B.	0 to 80 cm	**3380 ± 200**
L-421A.	240 to 300 cm	**4130 ± 200**

L-389A. Atlantis Seamount **8600 ± 350**

Lithified carbonate material (A152-Dr108) dredged from the surface of the Atlantis Seamount (34° 09′ N Lat, 30° 14′ W Long) at a depth of about 540 m. Sample was one of a large number of cobbles dredged up. Coll. 1948 by M. Ewing; subm. by B. C. Heezen, Columbia University.

B. Caribbean Sea

L-430C. Cariaco Trench, Atlantic Ocean **10,730 ± 250**

Organic material from a depth of 440 to 450 cm in a core (V-12-97) taken in the Cariaco Trench (10° 35′ N Lat, 65° 04′ W Long) N of Venezuela. Sample comes from just above contact between an organic-rich muck, which forms the upper portion of the core, and steel-gray organic-free clay. The sample should date the time of stagnation of the trench. Coll. 1957 and subm. by B. C. Heezen. *Comment*: a modern control value 3.2% less than age-corrected 1890 oak wood was used in the age calculation. This figure is based on the average C^{14}/C^{12} ratio for dissolved bicarbonate in Caribbean surface water together with a correction for an assumed 3.5% discrimination against carbon-14 during the formation of the organic material.

C. Mediterranean Sea

L-392. Mediterranean Sediment Core

Samples from a large-diameter (8 in.) core (V-10-LDC64) taken at a depth of 1167 fathoms in the Mediterranean Sea (34° 23′ 30″ N Lat, 24° 6′ 9″ E Long). The core contains a layer of organic-rich material overlain by several layers of organic fill-sediment. Coll. 1956 by M. Ewing; subm. by R. Menzies,

L-392A. 8 to 15 cm, fine **5650 ± 400**
Fine fraction (<74μ) calcium carbonate from a depth of 8 to 15 cm.

L-392B. 8 to 15 cm, coarse **5870 ± 300**
Coarse fraction (>74μ) calcium carbonate from a depth of 8 to 15 cm.

L-392C. 23.5 to 28.5 cm, coarse **8700 ± 1000**
Coarse fraction (>74μ) calcium carbonate from a depth of 23.5 to 28.5 cm (the organic-rich layer).

L-392D. 23.5 to 28.5 cm, fine **7400 ± 200**
Fine fraction (<74μ) calcium carbonate from a depth of 23.5 to 28.5 cm (the organic-rich layer).

L-392E. 23.5 to 28.5 cm, organic **8400 ± 250**
Organic material from a depth of 23.5 to 28.5 cm (the organic-rich layer).

V. GEOLOGIC SAMPLES—MISCELLANEOUS

A. North America

L-372A. Lake Washington, Washington **5150 ± 200**
Fibrous peat from a core taken in the northern part of Lake Washington (47° 45′ 02″ N Lat, 122° 16′ 07″ W Long) 0.5 mi S of the mouth of the Sammamish River in the State of Washington. Sample is from the base of a 5-ft fibrous-peat layer, which overlies stratified sand and gravel and is overlain by 2 ft of limnic peat; obtained from 7 ft beneath the lake bottom and 27 ft beneath the lake surface. Since fibrous peat is a marginal lake deposit, the sample dates a lake level about 26 ft lower than now. The subsequent rise in level has resulted chiefly from building up of the Cedar River delta at the south end of the lake; the delta separates the lake from Puget Sound. Coll. 1955 and subm. by H. R. Gould, Humble Oil Company.

L-400A. Point Barrow, Alaska **3000 ± 130**
Arctic brown soil collected 1 mi S of the Arctic Research Laboratory (71° 20′ N Lat, 156° 36′ W Long), Point Barrow, Alaska. Sample taken from the A_1 horizon, 1 to 5 in. thick. Tedrow and Douglas (1958) conclude that the soil was formed in place and that the great sample age indicates equilibrium with the environment; hence little likelihood of podzol development with time. Profile description is given by Drew and Tedrow (1957). Coll. 1956 by L. A. Douglas, subm. by J. C. F. Tedrow, Rutgers University. *Comment*: sample was treated for humic-acid removal. Enough humic acid was recovered for dating.

L-400A. Residue after humic-acid removal **3000 ± 130**
L-400A. Humic acid **2100 ± 180**

L-400B. Gubik Formation, Alaska **10,900 ± 350**
Upland tundra soil included in Pleistocene Gubik sediments 1 mi S of the Arctic Research Laboratory (71° 20′ N Lat, 156° 37′ W Long), Point Barrow, Alaska. The site is about 20 ft above sealevel. Sample taken from organic-rich layer, 23 to 24 in. thick, which is about 1 ft down in the permafrost. Drills and explosives were used in sample collecting. Tedrow and others (1958) and Tedrow and Douglas (1958) suggest some possible origins. Coll. 1956 by L. A.

Douglas, J. C. F. Tedrow, and J. O'Sullivan; subm. by Tedrow. *Comment*: sample was treated for humic-acid removal and enough humic acid was recovered for dating.

L-400B. Residue after humic-acid removal **10,700 ± 350**
L-400B. Humic acid **11,050 ± 350**

L-400C. Umiat, Alaska **8720 ± 200**

Organic matter from upland tundra soil profile located 2 mi N of the Umiat Air Strip (69° 23′ N Lat, 152° 11′ W Long), Alaska. Site is approximately 360 ft above the Colville River. Sample taken from a 46 to 48-in. layer which is permanently frozen, in which ground ice comprises over 50% of the volume, and below which organic matter is absent. Drills and explosives were used in sample collecting. Tedrow and others (1958) and Tedrow and Douglas (1958) suggest some possible origins. Coll. 1956 by J. C. F. Tedrow and L. A. Douglas; subm. by Tedrow. *Comment*: sample was treated for humic-acid removal and enough humic acid was recovered for dating.

L-400C. Residue after humic-acid removal **8720 ± 200**
L-400C. Humic acid **5400 ± 180**

L-418A, B. Sandy Cay, Bahama Islands

Oölite sand from an intertidal area 3.25 naut. mi N 7° E of Sandy Cay (79° 12′ N Lat, 25° 28′ W Long), Bahama Islands. The oölites average 0.42 mm in diameter and consist of cryptocrystalline aragonite nuclei surrounded by concentric layers of aragonite. Coll. 1957 by E. Purdy; subm. by N. Newell and J. Imbrie, Columbia University. *Comment*: D. Thurber of the Lamont staff isolated sample fractions by acid leaching. Ages were computed using the average C^{14}/C^{12} ratio in N. Atlantic surface water as a control. This is 1% above age-corrected 1890 oak wood.

L-418A. Surface **225 ± 100**

Surface layer (first 10% removed by acid leaching).

L-418B. Nucleus **2350 ± 100**

Nucleus (residual material after 80% had been removed by acid leaching).

L-418C. Great Bahama Bank, Bahama Islands **1650 ± 100**

Oölite sand from beneath 20 ft of water in the northwest lobe of the Great Bahama Bank about 22 mi SE of Orange Cay (78° 48′ N Lat, 24° 46′ W Long), Bahama Islands. The oölites average 0.3 mm in diameter and consist of cryptocrystalline aragonite nuclei surrounded by concentric layers of aragonite. Coll. 1957 by E. Purdy; subm. by N. Newell and J. Imbrie. *Comment*: ages were computed using as a control the average C^{14}/C^{12} ratio in N. Atlantic surface water. This is 1% above age-corrected 1890 oak wood.

L-418D, E. Andros Island, Bahama Islands

Aragonite ooze from a 30-in. core (A-3) taken on the west coast of Andros Island (78° 17′ N Lat, 24° 46′ W Long) in the Bahama Islands. Although now 2 ft above sealevel, the material was probably deposited in shallow water. Coll. 1957 by J. Imbrie; subm. by N. Newell and J. Imbrie. *Comment*: ages were

computed using as a control the average C^{14}/C^{12} ratio in N. Atlantic surface water. This is 1% above age-corrected 1890 oak wood.

L-418D. 0 to 3 in. (top) **2330 ± 100**

L-418E. 27 to 30 in. (bottom) **2660 ± 100**

L-425. Labrador Iron Ore Deposit **>40,000**

Lignitized wood removed from iron-ore deposit in Ruth Lake Ore Body (54° 48′ N Lat, 66° 50′ W Long), Labrador, Canada. J. L. Usher believes wood to be either *Populus* or a member of the family Cupressaceae. Fossil leaves accompanying the wood identify it as late Cretaceous or early Tertiary, but well-preserved nature of the organic material first suggested a much younger age. Coll. 1956 by Iron Ore Company of Canada; subm. by J. L. Usher, Queen's University. *Comment*: sample was treated for humic-acid removal.

B. Europe

L-362. Thera Island, Greece **3370 ± 100**

Charred wood from beneath the bottom pumice layer in a quarry (36° 25′ N Lat, 25° 25′ E Long) at Fira, Thera Island, Greece. Found with the wood were human bones and teeth and ceramic art objects, the latter indicating a civilization stage of 1800 to 1500 B.C. On the basis that the pumice (which charred the wood) resulted from a volcanic explosion accompanying or preceding the formation of Santorin Caldera, the age of the charred wood gives a maximum age for the caldera. Coll. 1956 and subm. by A. G. Galanopoulos, University of Athens. *Comment*: sample was treated for humic-acid removal.

VI. ARCHAEOLOGIC SAMPLES

A. North America

L-339. Greenwich, Connecticut

Shells and charcoal (associated with potsherds and other cultural material) from the Manakaway shell midden, located on the southeastern tip of Greenwich Point (41° 0′ 9″ N Lat, 73° 34′ 2″ W Long), Greenwich, Conn. Archaeologic details are discussed by Suggs (1958) and a complete report of the excavations (Bull. 29 of the Connecticut Archaeological Society) is in press. Coll. 1955 and subm. by R. C. Suggs, American Museum of Natural History.

L-339A. Charcoal **750 ± 130**

Charcoal from Hearth no. 1 on sterile till at the base of the shell midden. Associated potsherds are of the East River tradition, probably variants of the Bowmans Brook Stamped type.

L-339B. Shell **730 ± 100**

Oyster and clam shells from the 6- to 9-in. level, Unit N30 E55. Associated with potsherds of both the East River and Windsor traditions.

L-273. Smithfield, Virginia **<100**

Shingle from Old St. Luke's Church in Smithfield, Va. Church, constructed in 1632, is the only original Gothic church remaining in the United States. During the planning of the restoration the question arose whether the roof

shingles were the originals. The C^{14} measurements suggest that they were not. Coll. 1955 and subm. by J. G. Van Derpool, Columbia University.

L-377. Castle Windy, Florida **930 ± 100**

Charcoal from a depth of 10 ft in an Indian shell midden at the Castle Windy site (28° 53′ N Lat, 80° 48′ W Long) on the east side of Mosquito Lagoon 15 mi SE of New Smyrna Beach, Florida. Sample came from the base of the middle or "crushed coquina" zone. Associated pottery at all levels is of the St. Johns Check Stamped type. Regional chronology is described by Goggin (1952) and the site itself is described by Bullen and Sleight (in press). Coll. 1956 and subm. by R. P. Bullen and F. W. Sleight, Florida State Museum. *Comment*: other radiocarbon dates for the Castle Windy site are L-405A and B (this date list).

L-405. Castle Windy, Florida

Charcoal from each of two levels in the Castle Windy Shell Midden (28° 53′ N Lat, 80° 48′ W Long), Volusia County, Florida. Other archaeologic material found in the midden includes artifacts and shells together with animal, bird, and fish remains. The archaeology of this site is described by Bullen and Sleight (in press). Coll. 1957 by R. P. Bullen and F. W. Sleight, subm. by F. W. Sleight, Central Florida Museum.

L-405A. Charcoal from 18-in. level **650 ± 100**

L-405B. Charcoal from 14- to 17-ft level **910 ± 100**

Comment: another sample (L-377, this date list) from this site has been dated at 930 ± 100 years. Both the above charcoal samples were treated for humic-acid removal.

L-381C. Modoc Rock Shelter, Illinois **7000 ± 170**

Charcoal from a depth of 19 to 20 ft in the Modoc Rock Shelter (38° 3′ N Lat, 90° 4′ W Long) 2 mi N of the village of Modoc, Randolph County, southwestern Illinois. This site has been excavated to a depth of 26.5 ft; some five zones, all containing implements, have been delineated. This sample comes from within the next-to-bottom zone (II). The archaeology of this site, including several radiocarbon dates, is described by Fowler and Winters (1956) and Deuel (1957). Coll. 1956 by M. L. Fowler; subm. by T. Deuel, Illinois State Museum. *Comment*: sample was treated for humic-acid removal. Other radiocarbon dates for the Modoc Rock Shelter are reported by Libby (1954) and Crane (1956).

L-431C. Twenhafel Site, Illinois **1440 ± 100**

Unburned bone and teeth from the Weber Mound of the Twenhafel Indian Site (37° 40′ N Lat, 89° 31′ W Long), Illinois. Contemporary artifacts indicate the site to be Hopewellian. Coll. 1957 by M. L. Fowler; subm. by T. Deuel. *Comment*: CO_2 released by acidification of the bone was used in the age determination. In the age calculation, the modern count was obtained by increasing the age-corrected 1890 oak wood count by 1.9% in accordance with slight C^{14} enrichment in bone as reported by Rafter (1955).

L-385. Signal Butte, Nebraska

Contemporaneous bone-charcoal pairs from the Signal Butte paleo-Indian site (41° 48′ N Lat, 103° 54′ W Long), Nebraska. All samples are from the

lowest horizon, no. 1; within this horizon, level A is the lowest and level C the highest, while level B, separating them, is sterile. Kulp and others (1951) reported radiocarbon ages for other Signal Butte samples (L-104A,B) and gave several site references. Coll. 1956 by R. G. Forbis; subm. by W. D. Strong, Columbia University.

L-385B.	Horizon 1A, charcoal	**4550 ± 220**
L-385C.	Horizon 1A, burned bone	**3400 ± 150**
L-385D.	Horizon 1C, charcoal	**4170 ± 250**
L-385E.	Horizon 1C, burned bone	**2850 ± 350**

Comment: all samples except 385E were treated for humic-acid removal. The ages reported are consistent stratigraphically if the bone and charcoal samples are considered independently. But the difference between stratigraphically identical samples indicates that, despite pretreatment, one sample type is subject to ground contamination; owing to its porous nature, the bone is more likely to be in error.

L-347. Midland, Texas **20,400 ± 1200**

Carbon extracted from caliche found in the Scharbauer site (31° 55′ N Lat, 102° 12′ W Long) near Midland, Texas. Sample was buried 18 to 24 in. within the Gray Sand deposit which also contained fossil human remains. It appears that the caliche was used as fire bricks so that the included carbon was apparently produced by charring of fats and oils which seeped from food cooked by early man. Wendorf and others describe the site in *The Midland Discovery* (1955). Coll. 1955 and subm. by F. Wendorf, Museum of New Mexico. *Comment*: calcium carbonate from the caliche itself has an apparent age of 23,500 yr. Since the initial C^{14} concentration in caliche is difficult to estimate and since the caliche may be contaminated with more recent calcium carbonate, the caliche age is difficult to evaluate.

L-427. Chiapa de Corzo, Mexico **2730 ± 150**

Charcoal from an excavated pit outside Chiapa de Corzo (16° 42′ N Lat, 93° 01′ W Long), State of Chiapas, Mexico. Sample rested upon sterile sand at the base of a cultural deposit representing a mixture of the earliest and second earliest phases of the Early Pre-Classic at Chiapa de Corzo. Coll. 1956 by G. W. Lowe; subm. by T. S. Ferguson, New World Archaeological Foundation. *Comment*: this sample was treated for humic-acid removal. Other portions of this sample were dated by the Groningen Laboratory as follows: GRO-1172, 2885 ± 60; GRO-1512, 2770 ± 50 (Ferguson, personal communication).

B. South America

L-404A. Chanquillo, Peru **2300 ± 80**

Wood (*Pithecellobium* sp.) from a lintel in the hilltop fortress of Chanquillo (9° 30′ S Lat, 78° 15′ W Long), Casma Valley, Peru. According to D. Collier, this elaborate stone-walled structure was formerly thought to date from the Coast Tiahuanaco period (ca. A.D. 900). But the ceramic collection made at the site in 1956 included a substantial number of sherds that were not of Tiahuanaco type. They resembled instead the plain ware of the Puerto Moorin period in Viru Valley, which dates at about 500 B.C. Present evidence suggests

the reoccupation in the Tiahuanaco period of a structure first used during the late Formative stage. The lintel date indicates that the major construction occurred during the first occupation. Coll. 1956 and subm. by D. Collier, Chicago Natural History Museum.

C. Europe

L-340. Grotte du Renne Series, France

Charred-bone samples from an Upper Paleolithic cave (Grotte du Renne) near Arcy-sur-Cure (47° 37′ N Lat, 3° 43′ E Long) (Yonne), France. Coll. 1955 by A. Leroi-Gourhan; subm. by H. L. Movius, Jr., Harvard University.

L-340A.	Level V, Upper Périgordian	**11,400 ± 250**
L-340B.	Level VII, Aurignacian	**10,900 ± 250**
L-340C.	Level IX, Lower Périgordian (Châtelperronian)	**15,700 ± 400**
L-340D.	Level X, Lower Périgordian (Châtelperronian)	**15,350 ± 400**

Comment: Movius considers these ages too young. Samples L-340C and L-340D, he believes, should be greater than 35,000 yr in age, L-340B approximately 30,000 yr, and L-340A approximately 20,000 yr in age. Because of the small amount of material available, the samples were given no pretreatment. The C^{14} dates must thus be considered minimum ages.

L-399D. Grotte de la Garenne, France **14,200 ± 500**

Burned bone from a cave hearth (Foyer II) in Grotte de la Garenne, near Saint Marcel (46° 34′ N Lat, 1° 30′ E Long) (Indre), France. Sample found in an extension of the cave which had been separated from the main part by a rock sill; in the extension, conditions for preserving perishable materials were much better than in the main cave where the occupation layer was overlain by a thick rockfall. Since archaeologic materials are late Upper Paleolithic (Middle Magdalenian), the sample dating throws light on the age of the Magdalenian in Western Europe. Coll. by J. Allain; subm. by H. L. Movius, Jr. *Comment*: sample portions were treated in several ways for dating:

L-399D.	Bone carbonate	**9000 ± 220**
L-399D.	Untreated sample	**9000 ± 400**
L-399D.	Residue after removal of humic acid and bone carbonate	**14,200 ± 500**

Other dates from the Middle Magdalenian layer in this cave (main section) were obtained by Libby (1951) as follows: C-577, burned bone from a hearth, 11,109 ± 480; C-578, ashy material from same hearth as C-577, 15,847 ± 1200; C-579, burned bone originating outside above hearth, 12,986 ± 560. In addition, a date of the Late Magdalenian occupation at the Grotte de la Vache near Tarascon-sur-Ariège is relevant (L-336C, unpublished: 11,650 ± 200).

D. Africa

Kalambo Falls Series, Northern Rhodesia

In old lake beds adjacent to the Kalambo Falls (8° 35′ S Lat, 31° 15′ E Long) on the Kalambo River near the south end of Lake Tanganyika in North-

ern Rhodesia, Africa, Clark (1954, 1956) has discvovered a prolific archaeologic sequence extending from the Early Stone Age to historic times. Coll. J. D. Clark; subm. by H. L. Movius, Jr.

L-395B. Early Iron Age **1080 ± 180**

Charcoal with associated pottery from gray sands and clays near the middle of the Iron Age deposit (6.5 to 7.0 ft in depth) at Site A1. Since sherds throughout the deposit are essentially of the same type, the sample should roughly date the Channeled Ware culture. Because the date does not indicate the complete time range of the culture at this site, Clark's prediction (personal communication) that this culture extends back to between 1500 and 2000 B.P. is not inconsistent. *Comment*: date given above is for a sample portion treated for humic-acid removal. An untreated portion gave an age of 1010 ± 100.

L-399C. First Intermediate Culture—Sangoan
43,000 ± 3300

Wood from beneath the third occupation floor, i.e. under Middle Stone Age occupation and over Early Stone Age layers at Site A. Sample comes from the roots of a tree that apparently grew on a land surface developed on the lower levels of the Earlier Stone Age beds after the upper levels had been removed by erosion. The tree then was buried by material upon which the third or Middle Stone Age occupation floor developed. The sample is believed to date the time of the Sangoan Culture. *Comment*: sample was treated for humic-acid removal and enough was obtained for dating. The ages of the two fractions are based on three 1000-min measurements apiece. In both cases, all individual measurements exceed average background; in addition, both average net sample counts are three times the standard errors of the net counts. These ages are the oldest reported thus far by the Lamont Laboratory. Until additional fractions are isolated in an effort to study contamination further, these ages should be used in a conservative manner.

L-399C. Residue after humic-acid removal **43,000 ± 3300**
L-399C. Humic acid **42,000 ± 3000**

L-399A. First Intermediate Culture—Sangoan **>40,000**

Wood from a clay-filled gully cut in current-bedded sands and believed to be of approximately the same age as samples L-399C and L-399B. A finite date would fix the beginning of a rise in lake level provisionally identified by Clark (personal communication) as contemporary with the onset of the Gamblian Pluvial period. *Comment*: sample treated for humic-acid removal.

L-399B. First Intermediate Culture—Sangoan **>42,500**

Wood from the fourth occupation floor at Site B. Associated cultural material was sparse but sufficient (in the form of picks) to be sure that it is post-Chelles-Acheul and belongs with the Sangoan. The general agreement among samples L-399A, B, and C indicates a date in the region of >40,000 for the Sangoan Culture. In addition, if the beds containing the Acheulian Culture floors are of Kanjeran age rather than of early Gamblian age, the same date holds for the onset of the Gamblian Pluvial period. *Comment*: sample was first measured without treatment and a finite age was obtained. Sufficient material

was available for isolation of cellulose and lignin, however, and the age was then shown to exceed the Lamont dating range.

L-399B.	Untreated wood	**32,500 ± 2800**
L-399B.	Wood lignin	**>38,000**
L-399B.	Wood cellulose	**>42,500**

Floor 5 (Acheulian) in the Kalambo sequence has been dated as >35,000 (L-271A, Broecker and others, 1956) and as >52,000 by the Groningen Laboratory (Clark, personal communication).

L-399E. Grotte de Taforalt, Morocco **11,900 ± 240**

Charcoal from a hearth in Grotte de Taforalt (34° 49′ N Lat, 2° 24′ E Long), Taforalt, Morocco. Sample came from the top level which, with the two below it, represents the Oranian culture of Upper Paleolithic-Early Mesolithic times. Materials of the Mousterian culture are also present in the cave. Subm. by H. L. Movius, Jr. *Comment*: Lamont radiocarbon dates for the Capsian culture (thought to be essentially contemporaneous with the Oranian culture) are reported by Kulp and others (1952, L-133B, L-134), Broecker and others (1956, L-240B) and Broecker and Kulp (1957, L-240A); all dates fall between 6800 and 8400 yr B.P. Samples above and below L-399E have been dated by Centre Atomique de Saclay (Movius, personal communication); the sample above gave an age of 10,800 ± 400, the sample below 12,070 ± 400.

E. Pacific Islands

L-394. Marquesas Islands, French Polynesia

Charcoal from fire pits in two sites in Uea valley or Bay Marquisien on the southwestern coast of Nuku Hiva (8° 56′ S Lat, 140° 11′ W Long). Both sites are small rock shelters, NBM-1 being situated at the base of the "Roche remarquable, 200 m. environ", shown on the south side of this valley on Map 3931, Service Hydrographique de la Marine, Paris, 1883, and NBM-5 being situated at the extreme south side of the beach. Archaeologic details are given by Shapiro (1958). Coll. 1956 by H. L. Shapiro and R. C. Suggs; subm. by Shapiro, American Museum of Natural History.

L-394F. Site NBM-1 Unit 55-5 **480 ± 100**

Charcoal resting on bedrock at a depth of 20 in. Simple and compound shank hooks are associated with the charcoal.

L-394J. Site NBM-5 Unit-X **270 ± 100**

Charcoal from base of large earth oven on bedrock at depth of 36 in. Associated with simple hooks.

VII. CHECK SAMPLES

L-292. Groningen, Netherlands **1250 ± 150**

Wood from the Walburg Church in Groningen (53° 12′ N Lat, 6° 36′ E Long), Netherlands. This sample has been used as a standard for interlaboratory comparison. The Groningen radiocarbon laboratory (de Vries and Barendsen, 1954) has obtained an average age about 1000 yr based on a large number of measurements. Coll. 1950 and subm. by Hl. de Vries, University of Groningen. *Comment*: the difference in the Lamont and Groningen ages results

largely from the fact that no Suess-effect correction was applied to the Groningen age. According to de Vries, such a correction would raise his age to about 1200 yr (personal communication).

L-371E. Pompeii, Italy **1830 ± 50**

Carbonized bread from a storehouse of ancient Pompeii (40° 50′ N Lat, 14° 30′ E Long), Italy. Still retaining the appearance of a baker's roll that seemingly was overdone, the material was charred by the volcanic ash fall that buried the city in A.D. 79, roughly 1880 years ago. Although precise information is not available concerning how long grain was stored at that time, the consensus is that the period did not exceed 2 years. Hence, this sample provides an excellent historic check of the radiocarbon method of age determination. Supplied by A. Maiuri; subm. by J. Bird, American Museum of Natural History. *Comment*: in order to obtain the best possible modern control for use in the age calculation, freshly sprouted wheat and live poplar twigs were collected near Rome by L. Lodi on November 7, 1956. Identical radiocarbon contents and C^{13}/C^{12} ratios were found for the two materials. On this basis, it was concluded that the usual Lamont control, 1890 oak wood, was acceptable once a minor correction was made for a slight difference in C^{13}/C^{12} ratio between the oak and the twigs and wheat. As always, an additional 68 years were added to the calculated age in order to allow for the decay of radiocarbon in the 1890 oak wood.

L-423. Eniwetok Atoll, Marshall Islands

Carbonate material from drill holes in Eniwetok Atoll, Marshall Islands. Purpose of the radiocarbon age determinations was to provide a comparison with ages determined by the ionium-uranium method (Potratz, Barnes, and Lang, 1955).

L-423A. Parry Island **4900 ± 150**

Sample of cuttings from a 40- to 45-ft depth (no. E-1, 40-45) in drill hole on Parry Island (11° 24′ N Lat, 162° 22′ E Long), Eniwetok Atoll, Marshall Islands. Coll. 1952 by H. Ladd; subm. by H. Potratz, Washington University of St. Louis.

L-423B. Mujinkarikku Island **23,500 ± 1000**

Sample of cuttings from a 34 to 36-ft depth (no. Mu 7-13) in drill hole on Mujinkarikku Island (11° 39′ N Lat, 162° 15′ E Long), Eniwetok Atoll, Marshall Islands. Coll. 1950 by H. Ladd; subm. by H. Potratz. *Comment*: the corresponding ionium-uranium ages are 12,000 ± 4000 and 132,000 ± 10,000 respectively (Sackett, 1958). Most of the difference between the respective pairs is probably due to younger secondary calcite cementing the original aragonitic material. Recently obtained cement-free material will be run in the near future.

L-432. Interlaboratory Check **2200 ± 200**

Black-carbon sample sent by the Geochronology Laboratory of the University of Arizona. This had been dated by both Michigan and Arizona, and a 1500-yr difference obtained for the two measurements. Arizona's date was

3980 ± 160 (U.A. 21 and 22; Wise and Shutler, 1958), Michigan's date, 2400 ± 200 (M-540; Crane and Griffin, 1958). The Lamont measurement supports that of Michigan. Why Arizona's result was high is unknown. Fission-product contamination would produce the opposite effect; further, there seems to have been no overestimation of the sample carbon content. Currently, the Arizona laboratory is converting its system so as to measure CO_2 gas instead of solid carbon.

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CLAY MINERAL—CARBONATE RELATIONS IN SEDIMENTARY ROCKS*

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ABSTRACT. Mineralogical investigation of modern sediments off the coast of Peru and Chile reveals the presence of volcanic glass in many samples. The glass is commonly devitrified in sea water to fine aggregates of minerals, including calcite and kaolinite. The textural relations of these two phases suggest attainment of chemical equilibrium, and thus a thermodynamic analysis of their relationship is desirable.

A seven-component system, including the phases dolomite, calcite, chlorite, kaolinite, and quartz, is chosen for study. This system may be analyzed graphically if quartz is present in excess and H_2O and CO_2 are taken as "mobile" components. The expected phase associations under a given set of conditions are studied in detail and agree with existing petrographic data; the agreement shows that the hypothesis of chemical equilibrium among these phases in sedimentary rocks should be seriously entertained. The idea of incompatible relationship between calcite and kaolinite is reviewed and the evidences for it are not compelling.

Possible complications due to other clay minerals and other components are briefly considered. The most likely sources of trouble are montmorillonite and the mixed-layer clays. Depending on its composition, the montmorillonite may change the geometry of the phase diagrams but will not affect the calcite-kaolinite binary join. Whether the mixed-layer clays will change the diagrams depends on whether such clays behave as mono- or polyphase systems, about which nothing is as yet known.

INTRODUCTION

The physical-chemical relations among the minerals in sediments and sedimentary rocks have in the past received comparatively little attention. This neglect was probably due in part to difficulties in studying multicomponent systems, and in part to practical difficulties in phase identification, especially for the very fine-grained material. The problem of identification is amended by the rapid improvement of the Geiger-counter diffractometer since the end of World War II. A number of excellent studies are now in the literature.

To comprehend the mutual relations among the minerals, it is not adequate to study the mineral associations from composite samples, nor is it enough to study a few specific minerals in a given sample. Rather, the mineral phases that must be considered depend on the nature of the physico-chemical relations to be examined, and must be decided upon in each case. The present paper deals with certain of the observed mineral assemblages, and also theoretical possibilities and limitations, in systems involving carbonates and some clay minerals.

The clay mineral-carbonate systems are chosen for study, partly because of the data on hand, and partly because these, occurring commonly in fine-grained rocks, have the best chance of attaining chemical equilibrium. It is hoped that elucidation of their relations may also contribute towards a resolution of some controversial questions, for example whether a given clay mineral is an indicator of its environment of deposition or of the source area.

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MINERALOGY

Description of samples and experimental procedure.—Most of the samples studied are modern marine bottom deposits cored from the coast of Peru and Chile, by the research vessel *Atlantis* of the Woods Hole Oceanographic Institution, during the winter of 1955-56 (cruise no. 221). A number of the coring traverses extended from the shallow coastal waters across the Peru-Chile Trench (Zeigler, Athearn, and Small, 1957) to the "plateau" on the seaward side, thus enabling a study of the mineralogy of the cores with respect to their geographical location.

One of the interesting finds of the mineralogical study is the presence, in most of the samples, of variable amounts of volcanic glass mixed with the crystalline phases and fossil fragments. The glass grains are generally no more than 0.02 mm across. By a combination of index-of-refraction ($n \geq 1.57$) and density (≈ 2.7-2.8) measurements, most of the fresh fragments, which are olive green, are taken to be basalt (Wahlstrom, 1955, p. 287, 299) although other types, dominantly andesite but ranging to rhyolite, are also found (Zen, 1957b, p. 901). Much of the glass is devitrified to varying degrees with a concomitant decrease in density; in many cases the original glassy state of the grains is inferred when the grains enclose relatively fresh, commonly euhedral phenocrysts, generally hornblende and/or plagioclase in the andesine-labradorite range.

As it has not been practicable so far to separate the devitrified glass from the rest of the sample, due to the extremely fine grain size, x-ray study of the mineralogy is confined to the bulk samples. In these cases, microscopic examination of the samples under high magnification helps in correlating the nature of the x-ray mineralogy with the textural relations.

X-ray studies were made with a Norelco high angle Geiger-counter diffractometer. The techniques adopted have been described elsewhere (Zen, 1957b, p. 890). The -2μ fractions of the samples are prepared in the following way:

The sample (about 5 grams, because of the availability of material) is thoroughly stirred in a 100 ml graduated cylinder filled with distilled water. It is then allowed to settle for about 6 hours, and the top 13 cms of the liquid is decanted. If the sample does not deflocculate, more fresh distilled water is used until it does; no reagent is added. If the density of the grains is taken to be 2.5, Stokes' Law gives a maximum effective settling diameter equal to 1.3 microns for the fraction remaining in suspension. The suspended material is then centrifuged and thoroughly washed with distilled water, finally brought back to a milky suspension, transferred to glass slides and dried. Slides thus prepared show strong orientation of the platy minerals, suitable for x-ray identification. For each sample, four identical slides are made. The first slide is used as such. The second slide is saturated with ethylene glycol. The third slide is heated to

170-200°C for one hour, and the fourth slide heated to 450-500°C for one-half hour.

Criteria of mineral identification.—A large number of minerals encountered in the samples, such as quartz, plagioclase, calcite, dolomite, and halite (due to evaporation of the water trapped in the cores), have clear and distinct x-ray diffraction patterns and their identification and microscopic verification, even for fine-grained material, present little trouble. Such is not the case with the platy minerals. The criteria used for differentiating among the various groups of these have been set out before (Zen, 1957b, p. 890-892); since the writing of that paper, however, a number of modifications and improvements have been introduced. These are as follows:

1. Organic swelling of montmorillonite is now done with glycol rather than glycerin. Heating is done in the 450-500°C range rather than 550-600°C.

2. For chlorite-kaolinite differentiation, the criterion of Johns, Grim and Bradley (1954, p. 243) is adopted. The samples are heated to 450-500°C, and if the 7Å line is destroyed, it is taken to be chlorite; if weakened, a mixture of kaolinite and chlorite. This procedure is justified because kaolinite is known to be thermally stable under atmospheric conditions until *ca.* 600°C (Brindley, *in* Brindley, 1951, p. 57). Occasionally, a sharp 14Å line, revealed after glycol treatment has shifted the interfering montmorillonite line, remains after heating (the montmorillonite line is shifted to 10Å after this treatment). Such a line is interpreted as detrital chlorite whose thermal characteristics more nearly correspond to the data of Brindley and Robinson (*in* Brindley, 1951, p. 188) on well-crystallized material. No attempt has yet been made to differentiate non-swelling vermiculite from chlorite.

Phases resulting from devitrification.—With the combined x-ray and microscopic examinations, using the cited criteria, it has been possible to identify a number of phases resulting from the devitrification of glass[1], with varying degrees of confidence. Among the phases thus identified, quartz, calcite, a 10Å mica ("illite"), and an iron oxide (hydrous?) are definite. Microscopically, kaolinite is strongly suggested by a fine-grained, optically negative, platy mineral whose indices of refraction correspond to those of kaolinite (Grim, 1953, p. 279) and are not affected by the immersion media. Chlorite (optically positive) and an alkali feldspar are suspected but not confirmed. In the disaggregated material, there is no doubt of the presence of all the above phases, and in many of the very fine-grained bulk samples there is likewise no doubt of the above mineral assemblage.

PHASE RELATIONS

General considerations.—After a brief, general study of the choice of components and phases, the consideration of the phase relations between clay minerals and carbonates will be taken up in three parts. First, the relation between calcite and kaolinite will be studied in terms of the Phase Rule, and the existing hypothesis on their mutual relations reviewed. This will be followed by a study of a larger, seven-component system, which includes the minerals dolomite and chlorite as well as calcite and kaolinite. Mineral assemblages will be

[1] The textural relationships of the glass grains form studies by themselves and will not be pursued here.

predicted and compared with observations. Finally, the role of some other clay minerals will be briefly considered.

Gibb's Phase Rule, which relates the number of phases, ϕ, with the number of *independent* components, c, is:

$$w = c + 2 - \phi$$

where w, the variance or degrees of freedom, is the number of independent conditions that must be imposed on the system for its unique description. For a system in which c' components are "mobile" (i.e., values of their chemical activities[2] a are fixed independently of the bulk composition of the system), the variance is reduced,

$$w' = c + 2 - \phi - c'$$

(Korzhinsky, 1950, p. 52; Thompson, 1955, p. 80). For arbitrary values of the temperature and pressure, the maximum number of phases thus is

$$\phi_{max.} = c - c'$$

In our general four solid-phase system, seven components, reckoned as the oxides, must be considered. These are CaO, MgO, FeO, Al_2O_3, SiO_2, CO_2, and H_2O. As this is too many to treat graphically with convenience, the following simplifications will be used:

First, we may suppose that the chemical activity, a, of H_2O, is independently fixed, i.e., H_2O is a "mobile" component. This is consistent with observations on metamorphic rocks (Thompson, 1957, p. 844). For sediments and sedimentary rocks, the activity might be regarded as fixed by the composition of the sea water or ground water.

Second, we may do the same to the activity of CO_2. One might perhaps consider the value as that in an "average" atmosphere, a situation that would obtain and apply to the sediments if the sea water, say, is saturated with respect to atmospheric CO_2.

Finally, we might limit our study to systems in which some form of pure SiO_2 exists, thus eliminating the need to consider SiO_2 as a component (Turner, 1948, p. 50; Thompson, 1957, p. 843). In most cases this will be quartz. For some sediments, specifically many of the Peruvian samples, the presence of amorphous siliceous microfossil remains suggests that the limiting value of

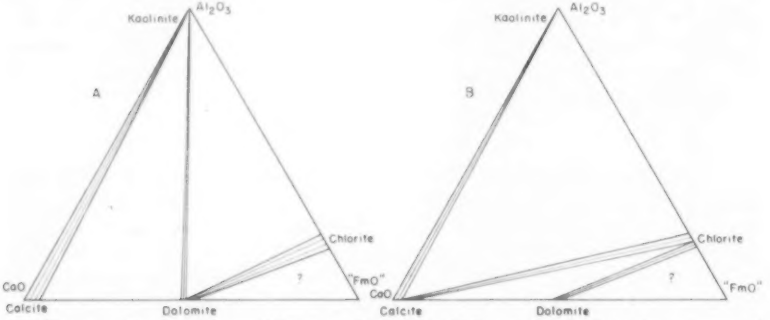

Fig. 1. Alternative assemblages in the system Al_2O_3—CaO—FmO in the presence of quartz and at particular values of T, P, a_{H_2O} and a_{CO_2}.

[2] Chemical activity is used in the sense of Lewis and Randall, 1923, p. 255.

a_{SiO_2} may be higher than that of quartz. Although amorphous silica may not have a fixed composition, due to its variable H_2O content and possibly adsorbed material, its fairly constant solubility in water (Siever, 1957, p. 824) indicates a narrow range of variation in a_{SiO_2} and may therefore be used as a metastable but reliable yardstick. It is doubtful that the differences between the solubilities of quartz and amorphous silica (Siever, 1957, p. 825-826), corresponding to a free energy difference of about 2 kcal/mole, will affect the stability of the silicate phases in equilibrium therewith.

We are thus left with four remaining "fixed" components, CaO, FeO, MgO, and Al_2O_3; if FeO and MgO are, for the time being, lumped together as "FmO", the system may be represented, at arbitrary values of T, P, a_{H_2O}, a_{CO_2}, and a_{SiO_2}, by a ternary diagram, figure 1, in which *A* and *B* depict two topologically distinct possibilities.

A few words may be said of the variations shown by the phases. The system calcite--dolomite has been recently studied (Harker and Tuttle, 1955; Graf and Goldsmith, 1955) and the compositions of these phases are extrapolations of the high temperature experimental data. These extrapolations should be qualitatively correct. Little is known of the composition of chlorite in sediments, and what is shown is the range observed in metamorphic rocks (Hey, 1954; Zen, 1955). It is assumed that this applies approximately to sediments. Again, this should be qualitatively correct. Finally, the "FmO" corner is left open as we are not sure of the appropriate phase. It may be siderite, serpentine, greenalite, or some other ferromagnesian phase.

To account for the observed mineral assemblages in terms of the phase diagrams, we presuppose of course that the system is at chemical equilibrium. It may be argued that for sedimentary minerals involving the silicates this does not obtain, and the argument is indeed difficult to reject with certainty. In some cases like the devitrifying glass, the assumption of chemical equilibrium seems justified. In Mesozoic and Paleozoic rocks, time is in favor of attainment of equilibrium, and the mineral associations are consistent with those in metamorphic rocks of comparable composition (Millot, 1950; Grim, Bradley, and White, 1957), where chemical equilibrium may be more completely attained. It is the bulk of the more recent sediments for which doubt is strong. In these cases, accord of petrographic data with the phase diagrams (and perhaps, in lucky instances, textural information) may be the best criteria of chemical equilibrium. If the mineralogy of a series of closely-spaced samples shows consistent correlation with that predicted from phase diagrams for the given chemical compositions, for instance, the suggestion is strong that the minerals in the rocks are in mutual equilibrium. Study of clay minerals by Grim indeed suggests (1958, p. 247, 249, 250) that these commonly adjust themselves to the depositional environment, although this conclusion is by no means held by all (Weaver, 1958, p. 255).

Calcite-kaolinite relationship.—The persistent association of calcite and kaolinite in the South American marine sediments is interesting, particularly as the apparent occurrence, in devitrified glass, excludes any possibility of organic or detrital origin for these phases. Assuming that they crystallized out of the glass *in situ*, in a marine environment, one may then inquire into their equilibrium relationships.

In the literature it is generally suggested (Grim, 1953; Millot, 1950) that kaolinite and calcite form a mutually incompatible pair; their mere co-occurrence is taken by some as sufficient evidence of chemical disequilibrium. Millot states that the presence of calcium ions in solution blocks the formation of kaolinite, and Grim considers that the high pH value necessary for calcite to form causes kaolinite to be unstable, where montmorillonite, illite, or chlorite form in its stead (1953, p. 351). The concepts of Millot and Grim may be discussed along the following lines:

1. Millot (1950, p. 288) considers that the presence of dissolved divalent ions, particularly calcium and magnesium, tends to block the formation of kaolinite. It is not clear whether he refers to a rate or an equilibrium process. It is clear however that dissolved calcium ions may not always be equated with the phase calcite; in fact for a given value of the chemical activity of CO_2 the presence of calcite severely limits the calcium ion concentration in a solution.

2. Although an increase in the pH value of the surrounding solution, *other things being equal*, may increase the solubility of kaolinite, it does not necessarily mean that the phase ceases to be stable, provided that the system is not an open one with respect to the material exchange of interest. We can, for instance, increase the solubility of halite by raising the temperature, but the solid halite remains intrinsically stable in its saturated solution.

3. Millot (1950, p. 284; see also Grim, 1953, p. 351) considers that a given cation concentration causes the flocculation of an alumina sol more readily than it does a silica sol. He uses this concept to predict the formation of kaolinite in an environment of low cation concentration, and of montmorillonite, for example, in one of relatively high concentration, with the ultimate control apparently the concentration of colloidal silica and alumina remaining as sols. In an analogous way (Millot, 1950, p. 283) he considers the effect of pH on the resulting clay mineral phase. It is clear however that these con-

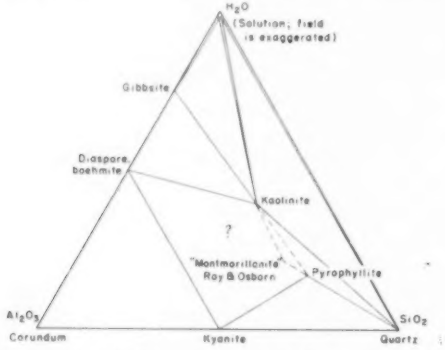

Fig. 2. Schematic and partial representation of the system H_2O—Al_2O_3—SiO_2.

siderations pertain largely to rates of processes, and cannot apply to equilibrium properties. As a matter of fact, reference to figure 2 shows that, accepting the compatibility of kaolinite and quartz, the pair solution—Al montmorillonite (after the formula of Roy and Osborn, 1954, p. 869) cannot be stable at all.

Natural montmorillonites all contain other components in addition to Al_2O_3, SiO_2, and H_2O, and therefore do not necessarily belong to the systems of sols that Millot considers.

4. Phases or groups of phases such as illite, chlorite, and montmorillonite, contain components other than Al_2O_3, SiO_2, CaO, H_2O, and CO_2, and so considerations of the compatibility of calcite and kaolinite as such cannot include these phases as alternatives; much larger and more complex systems must be taken into account. On the other hand, it is true that in the presence of sea water a phase like kaolinite *might* cease to be stable, either due to the desiccating effect of the saline water or due to chemical reactions forming a phase like illite. This point can be settled unequivocally only through laboratory studies; however, petrographic data do not indicate that this is true, at least in all cases.

5. There is a considerable body of petrographic data, both from modern sediments and consolidated rocks, supporting the common co-occurrence of the calcite-kaolinite pair. Of the 19 Mesozoic samples of marine sedimentary rocks studied by Millot (1950, p. 130-173), for example, 16 cases of this pair are reported; of the 18 samples of Mesozoic and Cenozoic lagunal deposits, 8 cases (*ibid*, p. 178-222). Other petrographic data will be presented later.

It is not claimed that calcite and kaolinite, wherever found, are stable together, or that sediments and sedimentary rocks are always equilibrium systems. Rather, it is suggested that existing petrographic evidence is compatible with the hypothesis of equilibrium, and that arguments advanced against this hypothesis might be open to alternative interpretations. In particular, the Peruvian sediments, as a whole, certainly are out of chemical equilibrium, as attested by the existence of volcanic glass; its devitrification nonetheless indicates that chemical reactions are taking place and thus equilibrium is being approached. Moreover, if two phases, here calcite and kaolinite, demonstrably result from devitrification, it is reasonable to suppose that locally, at least, chemical equilibrium is attained. The basic assumption here is that each phase is in equilibrium with its surrounding sea water with which material exchange is known to have occurred, and that diffusion of material in the water phase is sufficiently rapid that no sensible chemical gradient is set up on the scale of a devitrifying grain.

The problem may be alternatively formulated in terms of our general approach outlined earlier. The system involving calcite and kaolinite involves five oxide components, CaO, Al_2O_3, SiO_2, H_2O, and CO_2. Consistent with the simplifying scheme, H_2O and CO_2 are taken to be "mobile" components in a marine environment and need not be considered, and quartz is presumed to be present. Two components, CaO and Al_2O_3, remain, and the corresponding solid phases are calcite and kaolinite. The question then is, are there other phases, within this same binary system, which might be stable under the same conditions of temperature, pressure, and activities of the "mobile" components? Phases that have correct chemical compositions are these: anorthite, zoisite or clinozoisite, lawsonite, pumpellyite, margarite, and probably some of the zeolites like chabazite and scolecite. To the writer's knowledge, no such zeolite is reported from sediments or sedimentary rocks, and it is improbable that the other phases listed above would be stable within the environment of marine sedimentation,

even though these minerals occur in many of the heavy mineral suites. Pyrophyllite is a possible alternative phase to kaolinite, but is not known in sediments. There appears to be no alternative to the calcite-kaolinite pair within the five-component system.

System involving the solid phases chlorite-kaolinite-calcite-dolomite.—In addition to the five components just considered, we might consider two additional components, FeO and MgO, thus enabling us to account for two more phases, chlorite and dolomite. H_2O and CO_2 are again taken to be present in excess. By lumping FeO and MgO together—their separate effects will be considered shortly—pseudoternary diagrams may thus be constructed. Two alternative diagrams are presented in figures 1A and 1B; each diagram displays two 3-phase assemblages, separated by 2-phase fields, all in addition to quartz and an aqueous phase. Each of the 3-phase fields is invariant, i.e., the phases at apices of the fields are fixed in compositions, under arbitrary choices of T, P, a_{SiO_2}, a_{H_2O}, and a_{CO_2}, as well as of the bulk Fe:Mg ratio. There is considerable petrographic evidence to support the arrangement of the fields. Thus, in the Peruvian samples, calcite-chlorite-kaolinite (1B), as well as the three bounding 2-phase assemblages, are common. Calcite-dolomite-chlorite (1B) is suspected but as yet unconfirmed. Milliot's study of Mesozoic sedimentary rocks amply substantiates this diagram (1950, p. 130-173); this agrees with the calcite-dolomite-chlorite and calcite-chlorite assemblage from certain Ordovician rocks reported by Weaver and Bates (1952, p. 259) and Weaver (1953, p. 925-929; 935-939). Potter and Glass (1958, p. 35-39) also report the calcite-chlorite-kaolinite association with at least some of the kaolinite authigenic (p. 34). All these are in accord with the writer's study of some slates in Vermont, where the calcite-dolomite-chlorite assemblage is found.

On the other hand, both the works of Grim, Lamar, and Bradley (1937) and of Robbins and Keller (1952) on the clay mineralogy of Paleozoic limestones and dolomites show that the kaolinite-dolomite pair exists, corresponding to figure 1A. Unfortunately, it is not clear what the other mineral phases are in a given sample, for although the dolomite-kaolinite pair indicates *A*, the possible absence of quartz might negate our assumption of fixed a_{SiO_2}. It might also be desirable to apply more modern criteria on chlorite-kaolinite differentiation (W. D. Keller, letter, November, 1957). Among the more modern work, the dolomite-kaolinite association is reported by Bonython (1956, p. 83) and Rogers, Quirk, and Norrish (1956, p. 177-179). The association dolomite-chlorite-kaolinite has also been reported (H. D. Glass, 1957, oral communication).

Figures 1A and 1B are related by a reaction which may be schematically represented as follows,

$$\text{calcite} + \text{chlorite} + \text{carbon dioxide} = \text{dolomite} + \text{kaolinite} + \text{quartz} + \text{water} \qquad (1)$$

In this equation, the bulk Fe:Mg ratio, among other variables, is clearly significant in determining the assemblage, inasmuch as calcite, dolomite, and chlorite all show variability along this coordinate. This shows that to treat Fe and Mg as a single component is incorrect (Thompson, 1957, p. 846). One could show these relations more explicitly yet retain the ternary appearance of

the diagram by projecting from one of the phases in figure 1 (for a general discussion of this problem, see Thompson, 1957, p. 847). To aid visualization, a schematic representation of the four-component tetrahedron, A (kaolinite)- C (calcite)- F (siderite?)- M (magnesite?) is shown in figure 3; this is applicable at appropriate values of T, P, a_{H_2O}, a_{CO_2}, and in the presence of free

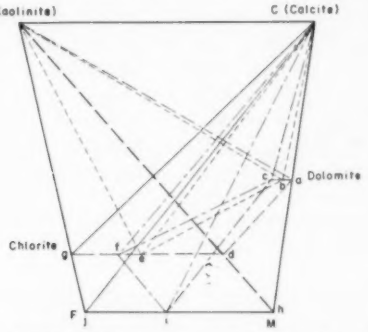

Fig. 3. The system A-C-F-M with quartz at particular values of T, P, a_{H_2O} and a_{CO_2}. The various volumes within the tetrahedron represent the following mineral assemblages:

C-c-i-f : calcite-chlorite-dolomite-siderite (?)
A-C-b-e : kaolinite-calcite-dolomite-chlorite
C-fg-ij : calcite-chlorite-siderite (?)
A-C-eg : calcite-kaolinite-chlorite
C-bc-ef : calcite-dolomite-chlorite
ac-hi-df : dolomite-magnesite-(?)-chlorite
A-C-ab : kaolinite-calcite-dolomite
A-ab-de : kaolinite-dolomite-chlorite

quartz. The 3- and 4-phase assemblages are given, and the letters, a,b,c, etc., indicate their compositional ranges. Chlorite is shown as more ferroferous than the coexisting dolomite; this is extrapolated from evidences found in slates, where chlorite of nearly unit Fe:Mg ratio coexists with nearly pure magnesian dolomite (Zen, unpublished data). At the high iron end, siderite and calcite are shown to coexist; this agrees with existing experimental information (Rosenberg and Harker, 1956, p. 1728) and the scanty petrographic evidence (Lippmann, 1955, p. 485; Potter and Glass, 1958, p. 35-39). Chlorite is assumed to be intrinsically stable over the entire Fe-Mg ratio range. For simplicity, all solid solution series are shown to have only one compositional degree of freedom, although in reality a phase like chlorite is known to show Al:(Fe,Mg) variations as well.

Two ternary projections of the tetrahedron, from calcite and kaolinite, respectively, are given in figure 4, *A* and *B*, on which the four 3-phase fields of figure 1 are indicated. It is evident that *all things being equal*, alternatives 1A and 1B may occur side by side, depending on the bulk Fe:Mg ratio.

We do not know enough about the intrinsic stability of chlorite under the contemplated conditions to warrant a representation of the situation should chlorite fail to show complete solid solution over the entire Fe:Mg range, a situation that might be indicated by the siderite-kaolinite pair reported by Potter and Glass. The necessary modifications to figures 3 and 4 are fairly

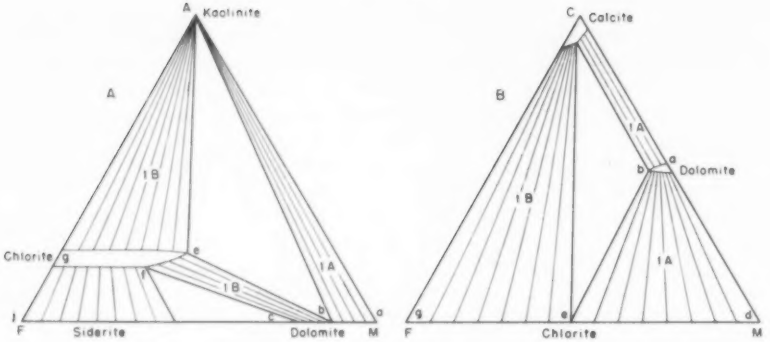

Fig. 4. Projections from the tetrahedron, A-C-F-M. (A), projected from calcite; (B), projected from kaolinite. Diagrams are highly schematic and assume the presence of excess quartz.

straightforward for such a case and the details will not be pursued. The problem is further complicated by the possibility of oxidation of ferrous minerals to form, for instance, oxy-chlorite; for this means that another independent variable, a_{O_2}, is to be introduced without new phases being added to the system. More empirical data, experimental, petrographic, and oceanographic, are needed for specific conclusions.

Finally, a few words may be said of the qualitative effect on the system of changing the values of the physical and chemical variables in addition to the effect of Fe:Mg ratio, just discussed. Reference to equation (1) shows that increases in a_{H_2O}, due, for example, to an influx of fresh water, as well as in a_{SiO_2} (which is assumed to be fixed by quartz, however) favor the calcite-chlorite pair, where increases in a_{CO_2} have the opposite effect, other things being equal. An increase in temperature favors the side of higher entropy content, but as thermochemical data on most of the phases are lacking, this effect cannot be evaluated.

A pressure increase (e.g., different depth of water) favors the side of lesser volume. The numerical values of ΔV, and even its sign, depend strongly on the state of aggregation of CO_2 and H_2O. Without going into the details, it may be said that, as limiting cases, if H_2O is liquid water and CO_2 is a gas (corresponding to a saturated solution of carbon dioxide), the volume of gaseous CO_2 is the predominating term. If the system is closed with respect to CO_2, pressure increases favor the kaolinite-dolomite pair. However, if the system is open to CO_2, whose activity is externally fixed, then an increase in total pressure favors the calcite-chlorite pair instead (Thompson, 1955, p. 80, eq. 19a). On the other hand, for a solution in which all the CO_2 hydrolyzes and dissociates into CO_3^{--}, pressure strongly favors calcite and chlorite due to the negative partial molar volume of H_2CO_3 (Zen, 1957, p. 116).

Role of other clay minerals

A. Montmorillonite.—Montmorillonite presents difficulties in graphical representation, largely because of its variable composition. Published analyses

(Ross and Hendricks, 1945; Kerr et al., 1950; see also Grim, 1953, p. 371) show that what is called montmorillonite may vary along *all* the compositional coordinates, partly through valence-coupled substitution and partly through ion exchange. It definitely does not lie in the seven-component system just considered. Roy and Osborn (1954, p. 869) have synthesized an Al-montmorillonite end member. Sand, Roy, and Osborn (1953, p. 341; see also Roy and Tuttle, 1956, p. 161) also made preliminary studies on the phase relations of Na-montmorillonite, and Roy and Roy (1955) on pure Mg-montmorillonite as well as Mg, Al-montmorillonite. Unfortunately, these do not correspond to natural montmorillonites at least in that alkali and/or alkaline earth elements in the exchange position are absent. The results of their preliminary studies therefore cannot be directly applied to natural systems.

The method of treatment in this paper is as follows. The formula of montmorillonite is taken to be

$$(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$$
$$\downarrow$$
$$Na_{0.33}$$

proposed by Ross and Hendricks (1945, p. 48) where the exchangeable Na position may be more commonly occupied by Ca (*ibid*, p. 40). Two cases may then be distinguished, depending on whether the presence of montmorillonite represents a *net* addition of a phase or not, in our seven-component system.

Case I. Montmorillonite is not a net additional phase. This situation would obtain if the montmorillonite contains appreciable amount of Na, and no other essential Na phase such as albite is present. The added component, Na_2O, is balanced by the added phase, montmorillonite, in the phase rule, and the phase diagrams already considered remain valid.

Case II. Montmorillonite is a net additional phase. This is the case if the system contains essential Na phases like albite, *or* if the montmorillonite has only Ca, Mg, or Fe in its exchangeable position. Graphically this situation can be handled, on the A-C-Fm diagram, by subtracting an amount of Al from the montmorillonite formula equal to the amount of Na (i.e., albite composition, since quartz is present in excess; see, in this connection, Thompson, 1957, p.

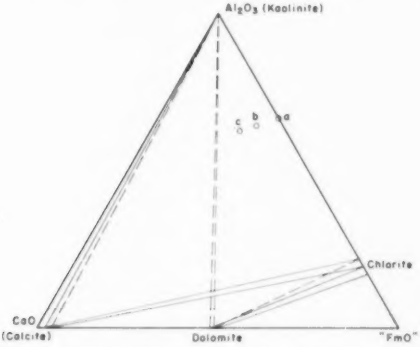

Fig. 5. A-C-Fm diagram showing composition of montmorillonite (points a,b,c) in relation to the system A-C-Fm. See text for explanations.

845) and recalculating the remaining Al_2O_3, CaO, and FmO to 100 percent. This is shown in figure 5, where the points a, b, c correspond to 1:0, 2:1, and 0:1 Na:Ca atomic ratio, respectively. The most notable feature of this diagram is that all the points plot well to the right of the kaolinite-dolomite 2-phase region; it does not at all enter into considerations of the calcite-kaolinite assemblage. Figure 6 gives schematic representations of the successive phase assemblages that must obtain to correspond to figures 1A and 1B. The transitions, from 6A to 6B, and 6B to 6C, are given, respectively, by the following reactions, assuming a 2:1 atomic ratio between Na and Ca:

$$\text{montmorillonite} + \text{calcite} + \text{carbon dioxide} = \text{kaolinite} + \text{dolomite} + \text{quartz} + \text{albite} + \text{water} \quad (2)$$

and

$$\text{montmorillonite} + \text{dolomite} = \text{calcite} + \text{chlorite} + \text{albite} + \text{quartz} + \text{water} + \text{carbon dioxide} \quad (3)$$

Mineral associations which are permitted by figure 1 but which are now in-

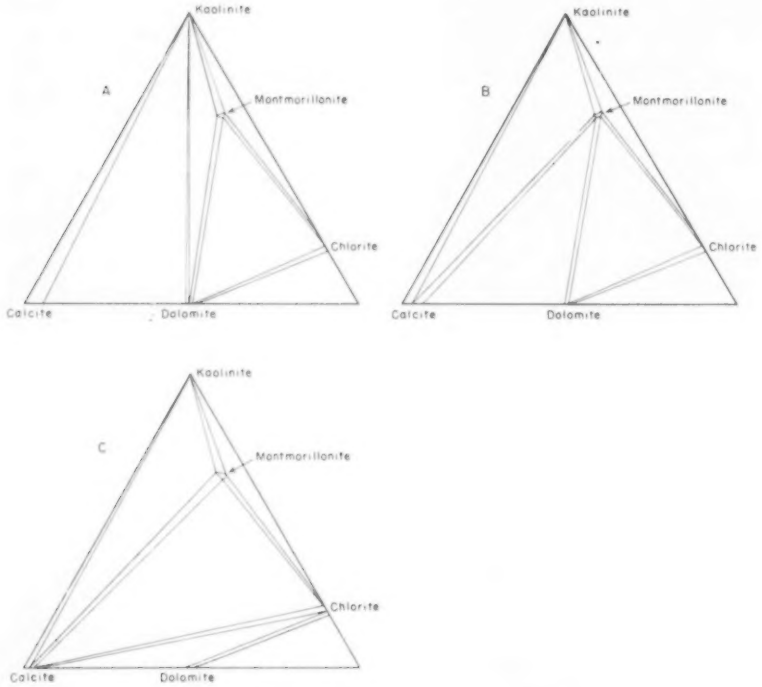

Fig. 6. The system A-C-Fm of figure 1, including montmorillonite. Figures A and C are analogues of figures 1A and 1B, respectively.

compatible are the 3-phase assemblages: dolomite-kaolinite-chlorite and chlorite-kaolinite-calcite. No 2-phase assemblages are affected by the net addition of montmorillonite as a phase in the seven-component system.

B. Other clay-mineral phases.—Illite is a common constituent of sediments and sedimentary rocks. It is, however, a phase in which potassium is an essential component, which is not part of our seven-component system. The equilibrium relationship of potassic phases, which include illite, potash feldspar, and phillipsite, constitute a study by itself and will not be pursued at this point; we only note that the presence of illite does not affect the preceding phase-equilibria considerations as such.

Vermiculite is an important phase in some sediments although it is not yet known from the Peruvian samples. Whatever its mode of origin, vermiculite may best be regarded for our purpose as a solid solution between K-biotite and Mg, Ca-biotite (see Barshad, 1948, p. 670). It therefore is another phase for which potassium is essential, and its discussion will be deferred until a later paper.

Mixed-layer clays pose a special problem. These clays occur commonly in many sediments and the constituent layers are largely montmorillonite, illite, chlorite, and vermiculite (Weaver, 1956). These individual constituents, as distinct phases, have all been referred to; the question is then whether a mixed-layer clay mineral behaves thermodynamically as a mono- or polyphase system. Roy and Roy suggest (1955, p. 173) that the occurrence of the discrete phases means that the appropriate mixed-layer phases must be metastable assemblages. Mixed-layer clays however may merely represent fine mechanical mixtures and connote no metastability, provided that the discrete phases are demonstrably *also* stable under the same physical and chemical conditions. Should some or all of the mixed-layer clays turn out to behave as monophase systems, of course, our phase diagrams will have to be drastically modified.

SUMMARY AND CONCLUSIONS

1. Study of some modern marine bottom samples shows the common coexistence of calcite and kaolinite, in addition to chlorite and quartz. At least some of these associations result from devitrification of volcanic glass and thus their mutual chemical equilibrium is suggested.

2. The arguments against the compatibility of calcite and kaolinite are reviewed. It is felt that these are not compelling, and the existing data are equally explanable in terms of chemical equilibrium as in terms of chance collection of detrital material.

3. An hypothesis of chemical equilibrium carries with it the implication that phase transformations may take place even at near-surface conditions, in a reasonably short time. Such transformations include major structural changes of the clay-mineral lattices. A clay mineral, therefore, may not be a reliable indicator of source material except insofar as the bulk chemical composition of the sediment must in some way reflect the bulk chemical composition of the material supplied. Should a detrital phase happen to be stable in the new environment, of course, it would not have to transform, even if the reactions should take place at rapid rates.

4. A seven-component system, involving the clay minerals chlorite and kaolinite, and the carbonates calcite and dolomite, is discussed in its general aspects, in terms of the Gibbs Phase Rule, and the phase assemblages predicted and compared with petrographical data. Alternative phase associations are shown to occur in sediments and sedimentary rocks, and the causes of the phase shifts are discussed. The possible effects of other clay minerals in this system are also considered.

5. Under favorable conditions, satisfied by many modern sediments, moderately complex, multicomponent systems can be successfully analyzed by thermodynamic methods. To make such an approach useful, however, detailed petrographic data are generally required, not only for specific minerals, but for the mineral *assemblages*. For it is often in the nature of these assemblages, rather than in any one particular mineral, that the clue to the environment of deposition lies. It is, therefore, hoped that in the future, petrographic reports on sediments and sedimentary rocks will emphasize the specific mineral associations, and wherever possible also the detailed mineral compositions and the textural relations among the phases, as these data are essential to a complete discussion of the mutual relations among them.

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TEMPERATURES OUTSIDE A COOLING INTRUSIVE SHEET

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ABSTRACT. Contact temperatures and temperatures in the country rock outside a cooling intrusive sheet are discussed, taking into account the effect of heat of solidification. It is shown that, for calculation of temperatures outside an intrusion, it is adequate to assume that the magma has a definite melting point instead of a melting range. On this assumption, contact temperatures, and temperatures in the country rock, are discussed with particular reference to dissimilar rocks. It is shown that the maximum temperatures attained in the country rock vary slowly with distance from the contact: the thin baked contact zones sometimes observed may be explained by pre-heating of the country rock for a short time before solidification commences. The theory is extended to cover the case of intrusion into wet sediments in which heat is absorbed by vaporization of pore-water, and calculated values of the contact temperature for a range of conditions are given. It is found in typical cases that a sheet is surrounded by a region of the order of half its thickness in which the country rock is heated in the presence of water vapor and vapor from the solidifying intrusion: beyond this to a distance of the order of the thickness of the sheet the country rock is heated in contact with vaporized pore-water; and beyond this again, it is in contact with heated pore-water only. The effect of movement of pore-water is also discussed approximately. The same theory applies to metamorphic reactions in the country rock, and the coking of coal is briefly discussed as an example.

INTRODUCTION

Many calculations of temperatures in and around intrusions have been made and used in attempts to estimate magmatic temperatures; these have been summarized by Lovering (1955). In particular, the effect of dissimilar rock conductivities on contact temperatures has been studied by Lovering (1936). In all this work, however, considerable uncertainty is introduced because the effect of latent heat is not adequately allowed for.

In a previous paper by Jaeger (1957), an exact theory was given on the assumption that latent heat was liberated uniformly over a specified range of solidification. The only difficulty in giving numerical results based on this theory is the large number of parameters involved: these include the initial temperature of the magma, its latent heat and range of solidification, and the thermal properties of liquid and solidified magma and country rock. In Jaeger (1957), in order to reduce the number of parameters, it was assumed that the magma was intruded at its liquidus temperature and that all materials concerned had the same thermal properties, and attention was concentrated on discussing the effect of latent heat and the width of the range of solidification on the contact temperature and the process of solidification. A further discussion of the process of solidification has been given by Jaeger (1958).

In the present paper the effect of dissimilar rock conductivities on contact temperatures and temperatures in the country rock will be studied in a general way, taking typical extreme values for the conductivities. The effect of vaporization of pore-water and reactions in the country rock will also be discussed. It is impossible to give complete results, and this is not necessary since for any particular intrusion it is a relatively simple matter to measure the actual rock conductivities and deduce a theoretical contact temperature from them on the assumptions stated below.

It was shown by Jaeger (1957) that while the liberation of latent heat has a very important effect on the contact temperature, the way in which it is liberated (i.e. the range of solidification of the magma) does not have a marked effect. For example, if latent heat of 100 cal/gm is liberated uniformly over ranges of 1000°–800°, 1000°–900°, and 1000°–1000° (the latter implying a fixed melting point of 1000°) the contact temperatures were found to be 617°, 621°, 622°, respectively. Such variations are not significant in the present state of knowledge, so in discussing temperatures in the country rock in more complicated cases it is legitimate as a first step to assume that the magma has a definite melting point T_1 and is intruded at this temperature (there is evidence, Walker, 1957, that in many intrusions the degree of superheat, if any, of the magma is small). This simplifying assumption may be applied, of course, only when temperatures in the country rock are being discussed: temperatures within the igneous rock are profoundly affected by the range of solidification. In this paper, temperatures in the country rock only will be discussed and the above assumption will always be made, but it may be remarked that the theory is easily extended to cover the case of superheated magma and a melting range.

The assumptions on which the calculations are based, and the notation used, are as follows:

1. The country rock is initially at a constant temperature, which will be taken as the zero of temperature, and at zero time, $t = 0$, magma is brought suddenly into contact with it (the case of pre-heating of country rock will be discussed later). After intrusion, it is assumed that there is no motion of the magma.
2. The magma has a definite melting point at temperature T_1 (relative to the country rock at zero temperature) and is intruded at this temperature. This is the simplifying assumption discussed above. The latent heat of fusion of the magma is L_1 cal/gm. The units used in numerical work will always be c.g.s., calorie and °C.
3. The country rock has thermal conductivity K_0, density ρ_0, specific heat c_0, diffusivity $\kappa_0 = K_0/\rho_0 c_0$, and solidified magma has corresponding values K_1, ρ_1, c_1, κ_1. These are all assumed to be independent of temperature. Step-function variations of thermal properties with temperature may be taken into account by the method described in connexion with reactions in the country rock.
4. The effects of transport of heat by volatiles from the magma and of convection in the magma will be neglected. As remarked by Jaeger (1957), they are probably not important in the present context.

CONTACT TEMPERATURES

Immediately after intrusion the temperatures at the contact takes the value T_c given by the formula below, and subsequently it decreases slowly. T_c is given by [Carslaw and Jaeger, 1959, §11.2(34),(37)]

$$T_c = \frac{\sigma T_1}{\sigma + \mathrm{erf}\lambda}, \qquad (1)$$

where λ is the root of

$$\lambda(\sigma + \text{erf}\lambda)e^{\lambda^2} = c_1T_1/L_1\pi^{1/2}, \tag{2}$$

and σ is the parameter

$$\sigma = \frac{K_1\kappa_0^{1/2}}{K_0\kappa_1^{1/2}} . \tag{3}$$

If latent heat is neglected, the initial contact temperature is just

$$\sigma T_1/(1 + \sigma). \tag{4}$$

Lovering (1936) has discussed contact temperatures and their variation with time for the case $L_1 = 0$. To illustrate the effect of latent heat, values of T_c calculated from (1) and (2) for $c_1 = 0.25$, $L_1 = 0$ and $L_1 = 100$, and various values of T_1 are given in table 1 for a selection of values of σ which cover the range likely to occur in practice. The thermal properties of typical rocks, taken from table 1 of Lovering (1936), are: "Quartzite", $K_0 = 0.0128$, $\kappa_0 = 0.031$; "Shale", $K_0 = 0.0019$, $\kappa_0 = 0.004$; "Coal", $K_0 = 0.0003$, $\kappa_0 = 0.002$; "Gabbro", $K_1 = 0.0043$, $\kappa_1 = 0.008$; "Granite porphyry", $K_1 = 0.0057$, $\kappa_1 = 0.009$. The contacts which will be considered are: "Granite porphyry—Coal", $\sigma = 3.35$; "Granite porphyry—Shale", $\sigma = 2$; "Gabbro—Quartzite", $\sigma = 0.66$; and the case $\sigma = 1$ in which $K_1 = K_0$, $\kappa_1 = \kappa_0$.

TABLE 1

Initial Contact Temperatures for Magma with a Fixed Melting Point T_1, Latent Heat of Fusion L_1, and Dissimilar Country Rock

σ	0.66		1.0		2.0		3.35	
L_1	0	100	0	100	0	100	0	100
$T_1 =$ 500	199	284	250	347	333	433	385	470
600	238	328	300	404	400	510	462	559
700	278	372	350	460	467	585	539	646
800	318	415	400	514	533	660	616	732
900	358	458	450	568	600	733	693	817
1000	398	500	500	622	667	805	770	901
1100	438	541	550	674	733	877	847	985

THE MAXIMUM TEMPERATURE ATTAINED AT A POINT IN THE COUNTRY ROCK

In the study of metamorphic reactions and of indicator minerals in the country rock it is of the greatest importance to know the maximum temperature T_m to which rock at a specified distance X from the contact has been raised. This depends on the thickness D of the sheet and the thermal properties of the magma and country rock. It is most convenient to plot T_m/T_c, the ratio of the maximum temperature to the initial contact temperature, as a function of X/D; this eliminates the gross effects of the variation of T_c given in table 1, but the curve so obtained still depends on σ, $(\kappa_1/\kappa_0)^{1/2}$, and the amount and method of liberation of heat of solidification. A number of such curves is shown in figure 1, and the essential point to be made here is that, having regard to the number and range of the parameters involved, the variation between the different curves is not large.

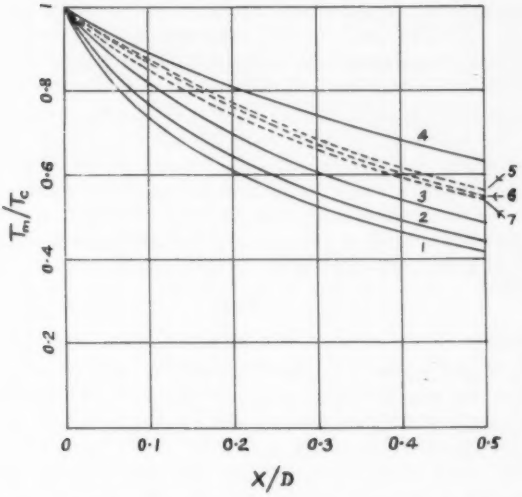

Fig. 1. The ratio of the maximum temperature T_m attained at distance X from the margin of a sheet of thickness D to the initial contact temperature. Curves 1 to 7 are for various values of the thermal properties and latent heat.

The curves numbered 1 to 4 in figure 1 and shown by full lines are calculated for the case of no latent heat and the values 3.55, 2, 1, 0.66 of σ from formulae given by Lovering (1936). They show that, as would be expected, maximum temperatures fall off more rapidly for lower values of K_0/K_1. When latent heat is taken into account, values of T_m have to be found by numerical solution of the equations of heat flow.

The dotted curves 5 to 7 of figure 1 are for the case of equal thermal properties of country rock and magma: Curve 5 is for $L_1 = 100$ and ranges of solidification 1100°–800° and 1000°–800°; Curve 6 is for $L_1 = 100$ and a definite melting point of 1000°; Curve 7 is for $L_1 = 80$ and a range of solidification of 700°–500°. Curves 5 and 7 have been read off from figures 1 to 3 of Jaeger (1957). The close agreement of Curves 5 and 6 provides additional support for the assumption made here that calculations for a definite melting point give an adequate description of temperatures outside the intrusion.

Comparison of Curve 3 with Curves 5 to 7 shows that for the case $\sigma = 1$ the effect of latent heat is to raise the values of T_m/T_c. It is reasonable to assume that this holds also for the case of dissimilar thermal properties. Thus figure 1 may be regarded as giving the extreme range of values of T_m/T_c likely to be encountered in practice. At a distance from the contact of 1/10 the thickness of the sheet, maximum temperatures range from 70 to 90 percent of the contact temperature, whilst at a distance of 1/100 of the thickness they are over 95 percent of the contact temperature. There is thus no *thermal* reason on the present assumptions for a thin zone of metamorphism near a contact. For example Dapples (1939) has reported a zone of coke 4 feet thick at the

margin of a porphyry intrusion 200 feet thick. He calculates that the contact temperature is 710°–728° and that the temperature 4 feet from the contact is 460°–500° which is consistent with anthracite not having been coked. In fact it appears from Curve 1 of figure 1, which has been calculated for this case, that a maximum temperature of 460°–500° will be attained at 40 feet from the margin. The inconsistency arises from the fact that Dapples calculated his contact temperatures using the results of Lovering (1936) for unequal conductivities, but for temperatures in the coal he used Lovering's (1935) results which assume equal conductivities and thus give temperatures which are far too low. To provide a layer of coke only 4 feet thick, minimum coking temperatures would have to be 670°–680°, or even higher if latent heat is taken into account.

INTRUSION INTO WET SEDIMENTS: INITIAL CONTACT TEMPERATURES

Previous work has been confined to the intrusion of magma into dry country rock. In the case of intrusion into wet sediments, heat will be absorbed by the vaporization of their pore-water and the intrusion will be surrounded by a region in which water is present in the vapor phase. The problem is complicated by lack of knowledge of the movement of pore-water and its vapor, and for simplicity we shall first consider the case in which there is no movement of pore-water, and its vapor is assumed not to transport heat by being condensed again at greater distances but to escape through fissures and to play no further part in the process.

With this assumption and those stated in the introduction, the problem for a single contact may be stated as follows: the region $x>0$ consists initially of magma at its melting temperature T_1, its latent heat of solidification being L_1; the region $x<0$ consists initially of wet sediments of porosity p. The boiling point of water at the prevailing pressure is T_0, its latent heat of vaporization is L_0 cal/gm and its density is ρ'. The initial temperature of the wet country rock is taken as the zero of temperature. The thermal conductivity, density, specific heat and diffusivity of solidified magma are as before K_1, ρ_1, c_1, κ_1, those of wet country rock are K_0, ρ_0, c_0, κ_0, and those of dry country rock are K, ρ, c, κ.

At time t after intrusion, the surface of separation of solid and liquid magma will be at $x = X_1$, the temperature there being the melting point T_1 of the magma; there will also be a surface of separation at $x = -X_0$ between wet and dry country rock, the temperature at this point being the boiling point T_0. Then a calculation similar to that of Carslaw and Jaeger (1959, p. 290), or Weiner (1955) shows that X_1 and X_0 are given by

$$X_1 = 2\lambda_1(\kappa_1 t)^{1/2}, \tag{5}$$

$$X_0 = 2\lambda_0(\kappa_0 t)^{1/2}, \tag{6}$$

where λ_1 and λ_0 are the roots of the simultaneous equations

$$\lambda_1 e^{\lambda_1^2}[q \operatorname{erf} \lambda_1 + \operatorname{erf} r\lambda_0] = q(T_1 - T_0)c_1/L_1\pi^{1/2}, \tag{7}$$

$$[T_0 e^{-\lambda_0^2} + (\lambda_0 pL_0 \rho'\pi^{1/2}/\rho_0 c_0) \operatorname{erfc} \lambda_0][q \operatorname{erf} \lambda_1 + \operatorname{erf} r\lambda_0] =$$
$$= s(T_1 - T_0)e^{-r^2\lambda_0^2} \operatorname{erfc} \lambda_0, \tag{8}$$

where $q = K\kappa_1^{1/2}/K_1\kappa^{1/2}$, $r = (\kappa_0/\kappa)^{1/2}$, $s = K\kappa_0^{1/2}/K_0\kappa^{1/2}$, (9)

and erfλ is the tabulated error function defined by

$$\text{erf}\lambda = \frac{2}{\pi^{1/2}} \int_0^{\lambda} e^{-u^2}\, du, \quad \text{erfc}\lambda = 1 - \text{erf}\lambda. \tag{10}$$

The temperature at any point can be expressed in terms of λ_0 and λ_1; in particular, the temperature T_c at the contact $x = O$ is given by

$$T_c = \frac{T_1 \text{ erf } r\lambda_0 + q\, T_0 \text{ erf } \lambda_1}{\text{erf } r\lambda_0 + q \text{ erf } \lambda_1}. \tag{11}$$

To get an indication of the effects of vaporization of water, the simple case in which wet and dry country rock and solidified magma are assumed to have the same thermal properties (so that $q = r = s = 1$) will be considered in detail.

Typical results for this case are shown in table 2. In all cases, unless explicitly stated otherwise, units are c.g.s., calorie and °C. The latent heat of solidification of the magma L_1 is taken to be 100 cal/gm. and two values, 1000°C and 700°C, have been taken for the melting point T_1. The density of all material has been taken to be 2.8 and the specific heat 0.25. Three values of the boiling point T_0 of water, namely 100°C, 200°C and 300°C, with latent heats of vaporization of 537, 462 and 334 cal./gm., respectively, corresponding to pressures of 1, 15.5 and 85.9 atmospheres, respectively (Birch, Schairer and Spicer, 1942, Table 14-5) will be considered. Finally, values of 0, 0.05, 0.2 and 0.5 will be taken for the porosity. The values of λ_0, λ_1 and T_c are given in table 2 for all combinations of these cases though some of them are rather unreal. The quantities D_s and t_s will be defined later.

TABLE 2

T_1	T_0	p	$L_0 p \rho'$	λ_0	λ_1	T_c	$1000 t_s/D^2$	D_s/D
1000	300	0.5	167	0.370	0.637	571	6.87	0.29
—	—	0.2	67	0.435	0.621	599	7.23	0.35
—	—	0.05	16.7	0.480	0.610	616	7.50	0.39
—	—	0	0		0.607	622	7.57	
1000	200	0.5	231	0.455	0.654	541	6.52	0.35
—	—	0.2	92	0.572	0.629	585	7.05	0.45
—	—	0.05	23	0.662	0.613	612	7.42	0.54
—	—	0	0		0.607	622	7.57	
1000	100	0.5	268	0.552	0.667	517	6.27	0.41
—	—	0.2	107	0.734	0.636	573	6.89	0.58
—	—	0.05	26.8	0.904	0.615	608	7.37	0.74
—	—	0	0		0.607	622	7.57	
700	300	0.5	167	0.226	0.532	425	9.85	0.21
—	—	0.2	67	0.273	0.517	444	10.43	0.26
—	—	0.05	16.7	0.305	0.507	455	10.85	0.30
—	—	0	0		0.503	460	11.02	
700	200	0.5	231	0.337	0.555	396	9.05	0.30
—	—	0.2	92	0.437	0.529	430	9.97	0.41
—	—	0.05	23	0.517	0.510	451	10.72	0.51
—	—	0	0		0.503	460	11.02	
700	100	0.5	268	0.451	0.574	370	8.46	0.39
—	—	0.2	107	0.621	0.539	417	9.60	0.58
—	—	0.05	26.8	0.786	0.514	448	10.56	0.76
—	—	0	0		0.503	460	11.02	

It appears from the results in table 2 that the lowering of the contact temperatures is not important for moderate values of the porosity and that its importance diminishes with depth.

The calculations of table 2 apply essentially to shallow intrusions at depths at which the pore-water pressure is less than the critical pressure. For pressures greater than this, the latent heat vanishes, but a sudden variation of specific heat with temperature may be taken into account by using the same formulae with $L_0 = 0$.

The case of unequal thermal properties of the various rocks and of movement of pore-water will be discussed later.

A SHEET OF FINITE THICKNESS INTRUDED INTO WET SEDIMENTS

Suppose that a sheet of thickness D meters at its melting temperature T_1 is intruded into wet sediments which are assumed to extend indefinitely on either side. Solidification will proceed inwards from both contacts in the manner described by (5), the magma between the planes of solidification remaining liquid at temperature T_1. The planes of solidification will reach the centre of the sheet at a time given by (5) with x equal to half the thickness of the sheet. This time of solidification t_s is given in years by

$$t_s = \frac{2D^2}{\lambda_1^2 \kappa_1} \times 10^{-3}, \tag{12}$$

approximately, where D is the thickness of the sheet in meters. During this time, the planes at which water is being vaporized will have moved outwards from the contacts a distance D_s meters given by

$$D_s/D = \lambda_0 \kappa_0^{1/2} / 2\lambda_1 \kappa_1^{1/2}. \tag{13}$$

Values of D_s/D and $1000t_s/D^2$ for the case of $\kappa_0 = \kappa_1 = 0.0071$ are given in table 2. For times greater than t_s the progress of cooling must be studied by numerical methods. Results for the typical case $T_1 = 1000$, $T_0 = 200$, $p\rho' L_0 = 92$, $L_1 = 100$, $K_1 = K = K_0 = 0.005$, $\kappa_1 = \kappa_0 = \kappa = 0.0071$, calculated by the method of Price and Slack (1954), are shown in figure 2. It appears that the plane at which water is vaporized continues to move outwards to a considerable distance which will be denoted by D_v, the temperature of the region $|x| < D_v$ finally falling below 200°C. It appears from figure 2 and table 2 that $D_s = 0.45$ D and that D_v is approximately 0.9 D or about twice D_s.

These distances D_s and D_v may be regarded as having some geological significance. The principal evolution of volatile gases from the magma takes place during solidification. Thus the country rock up to a distance of D_s from the margin will have spent a time of up to t_s years in contact with volatiles from the magma and water vapor from the pore-water, and will have been raised to temperatures of which those shown in figure 2 are typical. In the region at distances between D_s and D_v from the contact, the country rock will have been in the presence of water vapor from its pore-water, but at rather lower temperatures than those in the former region, while relatively few volatiles from the magma will be present. Finally, in the regions beyond D_v the pore-water will not have been vaporized, though it may have been maintained at temperatures near its boiling point for relatively long times.

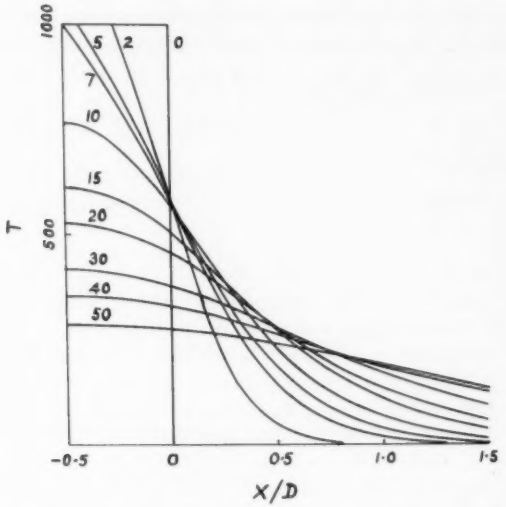

Fig. 2. Temperature T as a function of the distance X (meters) from the margin of a sheet with a fixed melting point of 1000°C intruded into wet sediments of porosity 0.2 in which the boiling point of water is 200°C. The numbers on the curves are times in multiples of $10^{-3}D^2$ years where D is the thickness of the sheet in meters.

UNEQUAL THERMAL CONDUCTIVITIES AND MOVEMENT OF PORE-WATER

In the previous discussion it was assumed for simplicity of presentation that all materials had the same thermal properties. In fact, dry sediments may be expected to have substantially lower thermal conductivity, density and specific heat than wet sediments and (usually) than igneous rocks, so that contact temperatures may be expected to be higher than those given in table 2. To see how important this effect may be, consider the special case of a sandstone of porosity $p = 0.2$ with $\rho_0 = 2.39$, $c_0 = 0.29$, $K_0 = 0.0060$, $\kappa_0 = 0.0086$ in the saturated condition, and $\rho = 2.17$, $c = 0.22$, $K = 0.0044$, $\kappa = 0.0092$ when dry, in contact with igneous rock for which $\rho_1 = 2.8$, $c_1 = 0.25$, $K_1 = 0.0050$, $\kappa_1 = 0.0071$. Then if $T_1 = 1000°$, $T_0 = 200°$, $L_0\rho'p = 92$, (5) to (11) give

$$\lambda_0 = 0.512, \lambda_1 = 0.609, T_c = 618°C, D_s/D = 0.46, \qquad (14)$$

which may be compared with the values $\lambda_0 = 0.572$, $\lambda_1 = 0.629$, $T_c = 585°C$, $D_s/D = 0.45$ of table 2.

Movement of pore-water will be determined by Darcy's law and geological conditions. It has been assumed above that it is vaporised without movement, but it is also possible to envisage circumstances in which the expansion of water on vaporization forces water away from the contact, or, alternatively, circumstances in which water vapor escapes readily and water moves towards the contact. Both these cases may be studied semi-quantitatively by extending the above theory to allow for change in volume on vaporization by the method

of Carslaw and Jaeger (1959), p. 290. The result is that if ρ' and c' are the density and specific heat of water, ρ'' is the density of water vapor, and

$$b = 1 - \frac{p\rho' c'}{\rho_0 c_0}\left(1 - \frac{\rho''}{\rho'}\right), \tag{15}$$

equations (5), (6), (7), (9), (11) still hold, and the only modification is that (8) is replaced by

$$\left[T_0 e^{-b^2\lambda_0^2} + (\lambda_0 p L_0 \rho'' \pi^{1/2}/\rho_0 c_0)\operatorname{erfc} b\lambda_0\right]\left[q \operatorname{erf}\lambda_1 + \operatorname{erf} r\lambda_0\right] =$$

$$s(T_1 - T_0)e^{-r^2\lambda_0^2} \operatorname{erfc} b\lambda_0. \tag{16}$$

If $\rho' = 0.86$, $\rho'' = 0.0079$ and the other constants are the same as in the above example, the solution is

$$\lambda_0 = 0.688,\ \lambda_1 = 0.571,\ T_c = 674°C,\ D_s/D = 0.66. \tag{17}$$

This is the extreme case in which no water vapor is assumed to escape: comparing (17) with (14) it appears that D_s and T_c have increased considerably. The values 674° of T_c is very little less than that (695°C) for the magma intruded into the same sediments in a dry condition.

The case previously discussed in which steam is removed as formed, there being no movement of pore-water, is equivalent in the present calculation to taking $\rho' = \rho''$, $b = 1$ in (15) and (16).

Finally, the effect of motion of pore-water towards the intrusion is equivalent to taking $\rho'' > \rho'$ in (15). For example, if $\rho'' = 2\rho'$, twice as much water as is contained in the pores is vaporized when the surface of separation between wet and dry sediments moves a small distance, and the pore-water moves towards the contact with the (variable) velocity $\lambda_0(\kappa_0/t)^{1/2}$. In this case, again with the values used above, the solution of (7), (11) and (16) is

$$\lambda_0 = 0.41,\ \lambda_1 = 0.64,\ T_c = 573°,\ D_s/D = 0.35. \tag{18}$$

Since this solution involves a variable velocity of the pore-water it does not correspond to any likely physical case, but it serves to indicate that velocities of this order do not have any very serious effect on contact temperatures.

METAMORPHIC REACTIONS IN THE COUNTRY ROCK

The theory given above is directly applicable to cases in which a metamorphic reaction takes place in the country rock at a definite temperature T_0. The reaction may be endothermic or (within limits) exothermic. In the latter case L_0 in (8) will be negative.

As an illustration, the question of the coking of coal by an intrusion may be considered to see whether a relatively low thermal conductivity of coke will substantially affect the width of the zone of coking. The exothermic heat of the coking reaction will be taken to be zero since its existence is doubtful (Lowry, 1945, p. 824). Taking $K = 0.0003$, $\kappa = 0.0014$ for the thermal properties of coke, and for coal and granite porphyry those quoted earlier, $T_1 = 800°$, $T_0 = 400°$, $L_1 = 80$ cal/gm., (7), (8) and (11) give

$$\lambda_1 = 0.256,\ \lambda_0 = 0.222,\ T_c = 754,\ D_s/D = 0.2.$$

It appears that the effect of assuming an extremely low value for the thermal conductivity of coke has little effect on the width of the zone of coking.

THE EFFECT OF PRE-HEATING OF THE COUNTRY ROCK

All the preceding calculations have been based on the assumption that at time $t = 0$, when the country rock is at a constant temperature, the magma is suddenly poured into it, like metal into a mould, and that heat transfer to the country rock and solidification of magma inwards from the contact begin instantaneously.

The essential point of this assumption is that solidification begins instantaneously, rather than that there is no subsequent movement of magma. In fact, on the assumptions of this paper, what happens in the liquid magma has no effect on the processes of solidification or heat flow in the country rock; so that liquid magma may move through or be added to the unconsolidated portion of the sheet at any time up to t_s of table 2, which, for a sill 100 m thick is of the order of 75 years. In fact magma has a melting range and not a fixed melting point, so that the above conclusions do not hold accurately but they suggest that later intrusions of magma into the unconsolidated portions of a sheet will have little effect, and flow of magma through the unconsolidated portions will merely be equivalent to assuming a higher (eddy) thermal conductivity for the magma.

The situation is entirely different if solidification does not begin at the instant $t = 0$. In this case it must be assumed that small elements of chilled magma are plucked from the surface and replaced by fluid so that the effect will be that the surface of the country rock is maintained at the magma temperature T_1 for some time t_0 before quiescent conditions occur at the surface and solidification can begin. The initial temperature of the country rock will then not be constant but

$$T_1 \operatorname{erfc} \frac{x}{2(\kappa_0 t_0)^{\frac{1}{2}}} .$$

This case cannot be treated exactly by the methods above, but to see the order of magnitude of the effect the simplest case in which latent heat is neglected and thermal properties are the same has been treated numerically. It is found that all points in the country rock to a distance of $1.2(\kappa_0 t_0)^{\frac{1}{2}}$, approximately, from the contact have been heated above the calculated contact temperature. For example, if $\kappa_0 = 0.01$ and $t_0 = 1$ day, this distance is 35 cm.

Thus a few days pre-heating of the contact surface may provide an explanation of the thin baked layers observed in some contacts. In such cases the temperatures in these layers lie between the "contact" temperatures calculated here and the temperature of the magma, but beyond these layers the results obtained above should hold.

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THE SIGNIFICANCE OF SCHNITTEFFEKT IN PETROFABRIC DIAGRAMS

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ABSTRACT. Peripheral girdles in petrofabric diagrams can be due entirely to the weak preferred orientation and inequidimensional shape of the minerals measured. This is termed *Schnitteffekt* (cut effect). A fabric analysis of a tectonite containing albite porphyroblasts with quartz inclusions shows that without thorough fabric analysis and the exercise of necessary controls, serious mistakes in interpretation can arise. Diagrams of the quartz inclusions showed similar patterns regardless of the direction in which the thin section was cut. Several controls by which mistakes due to *Schnitteffekt* can be avoided are suggested.

INTRODUCTION

The systematic analysis and typification of grain forms has not formed the subject of research in petrofabrics to the same extent as that of the optical orientation of minerals. It is difficult and sometimes impossible to determine accurately the shape orientation of minerals, particularly in the case of quartz. However, this can be done when the quartz is markedly inequidimensional. Such work is of fundamental importance to petrofabrics since grain shape can in certain cases affect the patterns obtained in fabric diagrams.

This was first pointed out by Winchell (1937). Work was subsequently carried out on a tectonite by Billings and Sharp (1937), who referred to the fact that peripheral girdles can be obtained in mica diagrams, due to the tabular habit of mica group minerals. Billings and Sharp also worked out a method for the correction of such diagrams of flaky minerals.

During the past few years, more and more attention has been paid to the pattern obtained in fabric diagrams caused entirely by the weak preferred orientation and inequidimensional shape of the minerals measured. In such cases the pattern is similar regardless of the direction in which the thin section is cut. This has been termed *Schnitteffekt* (Sander, Kastler and Ladurner, 1954) or literally translated "cut effect", and in this communication, the full significance of the *Schnitteffekt* concept in the interpretation of petrofabric diagrams is discussed. Several controls by which mistakes in interpretation due to *Schnitteffekt* can be avoided are mentioned by Sander, Kastler and Ladurner (1954) and the theoretical basis of its correction is also given. Correction tables for *Schnitteffekt* in flaky minerals and pencil shaped (*stäbchenformig*) minerals have been worked out by the above-mentioned Innsbruck workers (1957) but were first issued as a special publication in February 1958.

Work on the same problem was also carried out by Kaemmel (1955) who discussed the mathematical basis of the problem and whose conclusions and treatment of the subject do not differ greatly from those of the Innsbruck School.

These workers point out that the probability of a grain being included in a thin section is proportional to the distance between the planes tangent to the

grain and parallel to the plane of the thin section. In the case of grains with a rotation ellipsoidal form, this can be stated simply as a function of the angle between the grain axis and the thin section normal.

I. *Schnitteffekt in Mica Diagrams.*—Mica diagrams of a perfectly isotropic fabric will show a peripheral girdle even though no B-axis is present, due to the extreme tabular habit of the micas. The danger of drawing conclusions from uncorrected diagrams of flaky minerals has been clearly illustrated by the work of Sander, Kastler and Ladurner (1957), who have also shown that *Schnitteffekt* can be quantitatively corrected. They measured biotite flakes in three mutually perpendicular sections of a granite and found that in each case a peripheral girdle was obtained. Three mutually perpendicular B-axes did not occur in the rock, so the Kastler method[1] was devised for the correction of the diagrams. After correction only one B-axis was revealed by the diagrams, which were directly comparable to one another, when rotated, with the exception of diagrams cut perpendicular to the C fabric axis. These showed a large area of zero concentration in the centre, which therefore could not be corrected.

II. *Schnitteffekt in Quartz Diagrams.*—*Schnitteffekt* in quartz diagrams has not been previously described, although Professor Sander (personal communication) has known of its existence. However, recent research carried out by the writer at Innsbruck has demonstrated that *Schnitteffekt* can have a fundamental effect on quartz diagrams. An analysis illustrating typical results of this work is now described.

Quartz, internal and external in relation to albite porphyroblasts from a quartz-albite-mica-schist of the Dalradian of western Perthshire[2] was measured from three mutually perpendicular thin sections.

DESCRIPTION OF FABRIC DIAGRAMS

Figure 1a: *Quartz in internal in albite porphyroblasts.*—A well-developed cleft girdle is seen with a well formed *Kleinkreis* having a radius (as measured on a Schmidt net) of 30°. This diagram cannot be correlated with the external muscovite diagrams. The usual interpretation of this diagram would be that it shows a B-axis indicated by the cleft girdle and the existence of the previously unexplained *Kleinkreis*.

Figure 1b: *Quartz internal albite porphyroblasts.*—This diagram was made of a thin section cut perpendicular to the thin section corresponding to figure 1a and to the main S-plane in the rock. The diagram shows exactly the same pattern as figure 1a, that is, a well-formed *Kleinkreis* and a cleft girdle with radius of approximately 60-65°. Internal quartz measured in a third section cut perpendicular to the two previously described thin sections shows a similar pattern, that is, a cleft girdle and a *Kleinkreis*.

[1] A full account of this method and its mathematical basis is given in Sander, Kastler and Ladurner (1957, p. 404-408).

[2] On the eastern side of Ben More, 3½ miles East of Crianlarich (British Nat. Grid. Ref. NN/441242).

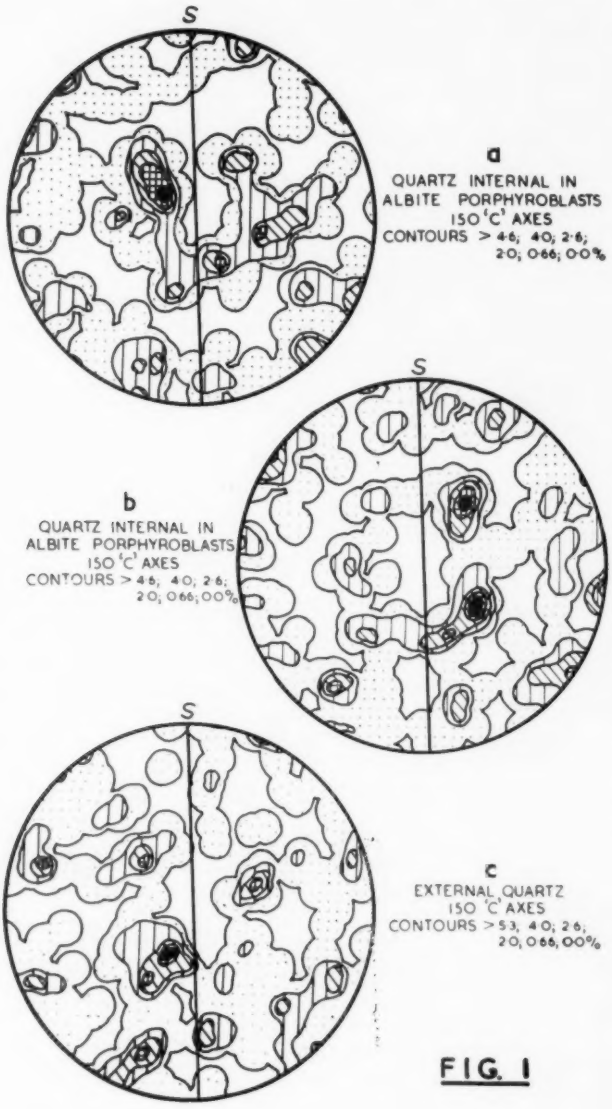


FIG. 1

These three diagrams cannot, on rotation and superposition, be correlated with one another or with any observable S-plane in the rock.

Figure 1c: *External quartz*.—This diagram is made from the same thin section as that of figure 1b. External quartz was analysed to see whether it bore any relationship to internal quartz. A minor cleft girdle is shown around the mica maximum perpendicular to the main S-plane, but the mica maximum lies near the centre of the small quartz cleft girdle at 30° to the main S-plane. The diagram shows a very weakly developed preferred orientation and no B-axis can be distinguished with certainty. Thus figures 1b and c from the same thin section, show a well-formed girdle and *Kleinkreis* of quartz in albite (1b), which vanished when the quartz is recrystallized i.e. external quartz (1c). In order to examine these features further the shape orientation of quartz was next examined.

OBSERVATIONS ON GRAIN SHAPE AND ORIENTATION

In the thin section corresponding to figure 1a internal quartz is sometimes preserved in helicitic minor folds in albite (plate 1A).
The quartz is sometimes elongated parallel to the outlines of the folds, which are clearly shown by trails of magnetite and epidote. Where, as in most cases, no helicitic folds are seen, quartz occurs in bands mostly parallel to the main external S-plane (plate 1B). About half the internal quartz grains are not clearly elongated and show an approximately equidimensional shape. In this section, all transitions between round and extreme elongate sections can be seen. External quartz shows, statistically, an imperfect equidimensional cross section but a slight elongation parallel to the S-plane can be noticed in some cases.

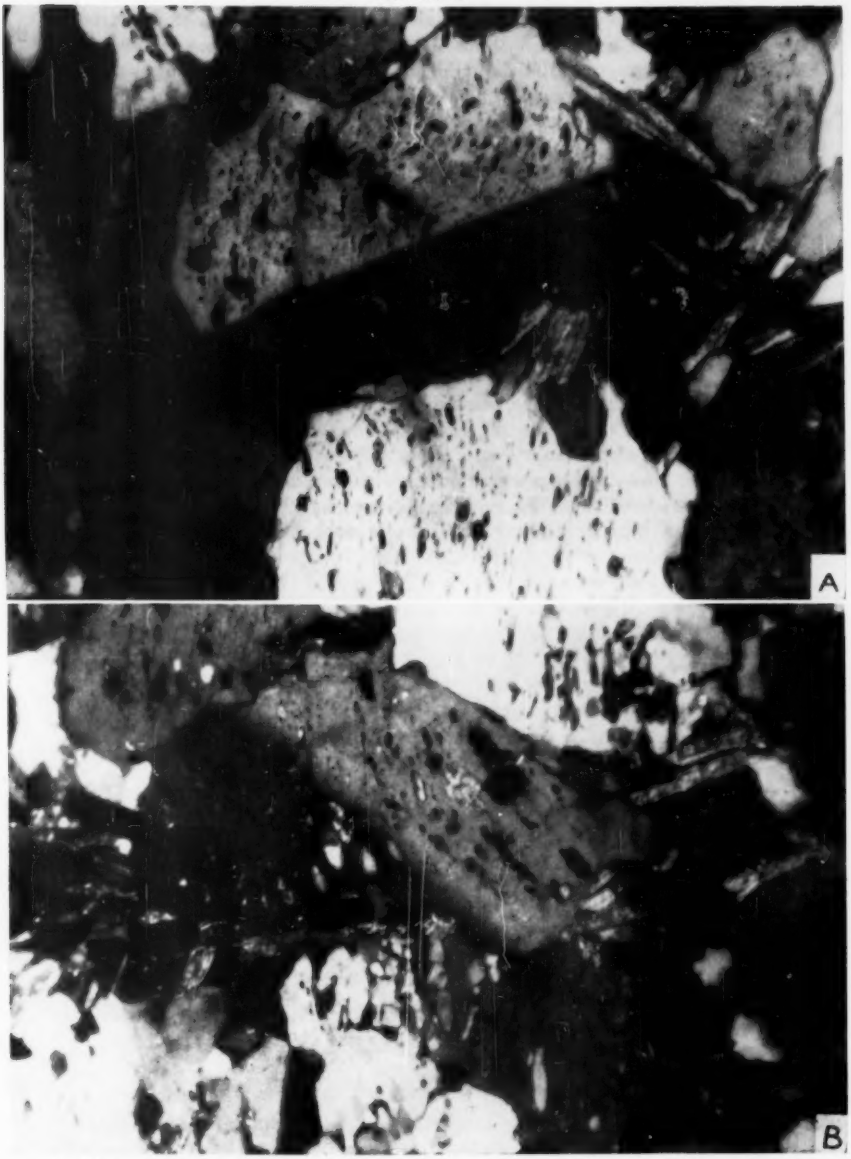
In the thin section corresponding to figure 1b, internal quartz in some cases is again elongated parallel to the internal magnetite and epidote trails and has approximately equidimensional shapes in many other cases. All transitions occur between very elongate and perfectly round outlines of quartz. No helicitic folds are seen in this section because the axis of these folds runs parallel to the plane of the section. External quartz shows a very similar pattern to that in the previously described thin section, i.e. approximately equidimensional in outline but a slight elongation parallel to the main S-plane in a few cases.

In the thin section perpendicular to 1a and 1b, that is, parallel to the statistically defined S-plane, internal quartz shows approximately the same outlines in the same proportions as in the other two thin sections. In most cases, the quartz inclusions show an orientation of maximum elongation directions parallel to the main lineation observed in hand specimen. This direction is parallel to the axes of the minor folds, the external folds, and those preserved helicitically in albite porphyroblasts. External quartz again shows predominantly equidimensional outlines in this section.

DISCUSSIONS OF DIAGRAMS IN RELATIONSHIP TO GRAIN SHAPE AND ITS ORIENTATION

The diagrams of internal quartz from three mutually perpendicular thin sections show a similar pattern and cannot, on rotation, be correlated with one another. This indicates that the diagrams cannot be explained by fabric

PLATE 1



A. Photomicrograph showing helicitically preserved flexures of the main foliation plane in albite porphyroblasts. (×100).

B. Photomicrograph of quartz inclusions in albite porphyroblasts. (×100).

heterogeneity, and that *Schnitteffekt* probably occurs. In order to confirm this it is necessary to measure the angle between the maximum elongation direction of quartz and the optic axis. However, in this particular case it is impossible to determine accurately the maximum elongation direction of the grains although an approximation can sometimes be made.

In the section cut approximately parallel to the S-plane, the apparent elongation axes probably represent the true maximum elongations more accurately than those apparent in the section perpendicular to the S-plane. This is because in the latter section the apparent elongation axes lying mostly parallel to this plane probably represent the trace of inequidimensional grains in the plane of the thin section.

In the former section, measurements of grains showing elongation directions at some angle to the fold axes have a much greater probability of being accurate than those having elongation parallel to the fold axes, since here the same considerations apply as in the case of sectors perpendicular to the S-plane. For example, a strongly inequidimensional grain lying in a flank, with its maximum elongation axis perpendicular to the axis of a minor fold, could show an apparent elongation direction, in thin section, parallel to the minor fold axis.

Bearing these considerations in mind the angle between the optic axis and the approximation to the maximum elongation direction, was determined in a hundred grains showing extreme elongation (length ÷ width ratio

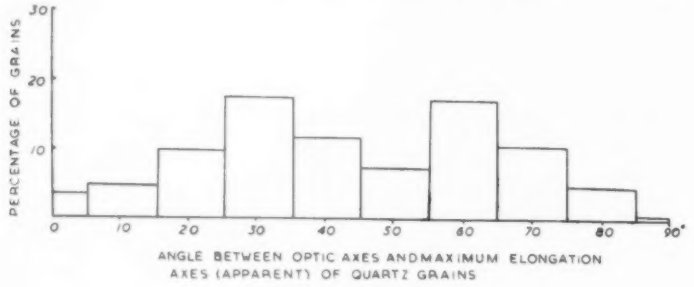


Fig. 2.

approx. 7 : 1) from a section cut parallel to the S-plane. The results, when plotted, show two maxima, one at approximately 30° and the other at approximately 60° (fig. 2). These correspond to the radii of the *Kleinkreis* and cleft girdle respectively.

Thus the results show that the *Schnitteffekt* hypothesis explains the cleft girdle and the previously unexplained *Kleinkreis* in this particular case.

CONCLUSIONS

The cause of *Schnitteffekt* in quartz diagrams is fundamentally the same as that in mica diagrams as quartz is rarely equidimensional or has a perfect preferred orientation. If the quartz were always perfectly equidimensional or had a perfect preferred orientation, no such *Schnitteffekt* could occur. How-

ever, quartz in tectonites is often elongated and the C-axis often lies perpendicular to the axis of elongation. When a thin section of a rock containing inequidimensional quartz grains is cut, those grains having axes of elongation normal to the plane of cut have a greater probability of being included in the thin section than those having axes parallel or at an acute angle to the slide. Thus *Schnitteffekt* can only give rise to a symmetrical pattern in the diagram. The diagrams show that even the commonly occurring *Kleinkreis* can be explained by *Schnitteffekt*. This was confirmed by measuring the angle between the optic axis and maximum observed elongation of a hundred quartz grains.

If a B-axis is thought to occur in the rock, the section should be cut preferably at 45° to the B-axis or even perpendicular to the C-fabric axis. The reality or otherwise of the B-axis can then be established since if a strong non-peripheral girdle results in the diagram, *Schnitteffekt* can be immediately excluded. Other controls which should, if possible, be exercised are:

1. The comparison of diagrams of various forms of the same mineral in any thin section, for example; small and large grains, internal and external grains, with respect to some host mineral, and the comparison of corresponding maxima and submaxima.
2. The measurement of two sections perpendicular or at forty-five degrees to one another and the rotation of one diagram to the position of the other. If it is found that the maxima and submaxima of the two diagrams then coincide, it is established that *Schnitteffekt* has not seriously affected the pattern obtained. If the diagram cannot be correlated, either the fabric of the rock is strongly heterogeneous or *Schnitteffekt* occurs. Heterogeneity can often only be proved by a type of fabric analysis termed *Achsenverteilungs-analyse* (Ramsauer, 1941; Sander, 1950).

The influence of inequidimensional grain shape on fabric diagrams can lead to grave mistakes in interpretation, particularly in the case of rocks with a low degree of preferred orientation. It must be emphasized that without thorough fabric analysis and the exercise of necessary controls, convenient and attractive assumptions concerning the interpretation of many diagrams are inadmissible.

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THE SYSTEM MAGNESIUM OXIDE-GERMANIUM DIOXIDE

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ABSTRACT. The phase equilibrium diagram for the system MgO-GeO_2 has been determined by the quenching method. Three compounds are found in the system: $MgO.GeO_2$, melting congruently at 1700 ± 20°C; $2MgO.GeO_2$; and $4MgO.GeO_2$, which dissociates at 1495 ± 10°C to $2MgO.GeO_2$ and MgO. A region of two-liquid immiscibility extends from 8 to 34 mole percent of MgO. Optical and x-ray data are given for the compounds, including a new monoclinic polymorph of $MgO.GeO_2$ which is analogous to clinoenstatite ($MgO.SiO_2$). This polymorph, apparently stable above 1555°C, inverts to the orthorhombic form (analogous to enstatite) with heating below that temperature. A protoenstatite phase was not observed, although a detailed study was not attempted. Important differences between the MgO-GeO_2 and MgO-SiO_2 systems are that no 4:1 silicate compound is known and that $MgO.GeO_2$ melts congruently at a much higher temperature than the incongruently melting metasilicate.

INTRODUCTION

Very little work has been reported on the high-temperature phase equilibrium relations of germania with other oxides. Throughout this paper germanium dioxide (GeO_2) will be referred to as germania. The present investigation constitutes the first report of a proposed systematic study of binary and ternary systems containing germania.

Germania is a glass-former similar to silica in that both have the same cation-oxygen ratio and tetrahedral oxygen coordination. One logical objective of the study of germania systems is to compare them with the corresponding silica systems. The MgO-GeO_2 system is of particular interest in this respect because of its possible bearing on problems of polymorphism in the system MgO-SiO_2.

Immiscibility in the MgO-GeO_2 system is of theoretical interest. From structural considerations, Levin and Block (1957) believe that the extent of immiscibility in corresponding silicate and germanate systems should be approximately the same. From this standpoint, the magnesia-germania system is of special interest because it represents the maximum extent of immiscibility to be expected with modifier oxides of divalent cations.

EXPERIMENTAL PROCEDURE

Preparation of Mixtures.—Starting mixtures were prepared in 3-gram batches from reagent grade MgO and spectrographically pure GeO_2 (quartz form). Each mixture was tumbled for 1 hour, ground for 1 hour in an agate mortar, and then pressed at 10,000-15,000 psi into pellets 5/8-inch in diameter. The pellets were calcined at temperatures up to 1150°C in platinum crucibles and then ground to pass a 200 mesh sieve. This process of pressing, firing and grinding, when repeated three times, gave an optically homogeneous mixture.

The pellets were weighed before and after each heat treatment in order to determine loss of germania by volatilization. Total weight loss was, in general, under 0.3 wt.%.

Quenching Experiments.—A conventional platinum-wound quenching furnace was controlled to ± 0.5°C with a self-adjusting, bridge-type controller, Levin and Ugrinic (1953), Mauer (1953). Temperatures were measured with a calibrated Pt-Pt 10 percent Rh thermocouple.

Because loss of GeO_2 becomes appreciable near liquidus temperatures, quench charges were sealed in capsules made from platinum or platinum 20 percent rhodium tubing (3 mm O.D. by 2.6 mm I.D.). Capsules were weighed before and after each quench experiment, inasmuch as differential loss of GeO_2 invariably accompanied capsule failure. Quenched samples were examined with binocular and petrographic microscopes and by x-ray powder methods.

Induction Furnace.—A graphite tube induction furnace was used to obtain the melting point of the compound $MgO.GeO_2$. The top of the tube was covered with a graphite disc having a central hole through which the sample suspension wire was passed. The sample, in a sealed capsule, was suspended in the center of the graphite tube. Temperatures were measured with an optical pyrometer sighted on the capsule through a ¼-inch hole in the wall of the susceptor. Nitrogen gas was passed through the susceptor to inhibit oxidation, since heating was done in air. Although the graphite was eventually oxidized, a number of runs were obtained with each susceptor.

The pyrometer was calibrated using diopside ($CaO.MgO.2SiO_2$), melting point 1391.5°C; and a 10:90 wt.% mixture of CaO and SiO_2, melting point 1708°C. The reproducibility of the method is ± 5°C. Samples were quenched in ice water by mechanical release of the sample suspension wire.

RESULTS AND DISCUSSION

MgO-GeO_2 Phase Diagram.—Figure 1 shows a composite equilibrium diagram of the system. The value 1855° ± 30°C for the congruent melting point of $2MgO.GeO_2$ was determined by Ringwood (1956). The 825°C inversion temperature of the 2:1 compound was determined by Dachille and Roy (1956). The melting point (1116°C) and inversion temperature (1007 ± 10°C) of GeO_2 were taken respectively from Laubengayer and Morton (1932) and Schafer and Roy (1956).

Fifteen compositions, as indicated in figure 1, were studied; over 150 individual quenching experiments were done. Only the most important data are shown on the diagram. In general, the points used to determine the liquidus curve are the average values of two quenching experiments within ten degrees of each other.

Considerable difficulty was encountered in determining the temperature and type of melting of the compound $MgO.GeO_2$. A number of runs were made using the graphite induction furnace. For a large percentage of the runs above 1675°C the Pt or Pt-Rh capsules failed. In these cases GeO_2 was lost differentially from the charge, resulting in the formation of large $2MgO.GeO_2$ crystals. When no loss of GeO_2 occurred, the 2:1 compound was not obtained. Therefore, congruent melting is indicated.

Another difficulty was the inability to quench the liquid of 1:1 composition to a glass. The charge quenched from above the liquidus always consisted of orthorhombic $MgO.GeO_2$ (low-temperature form). Within the limits of experimental error, the 1:1 compound was found to melt at 1700° ± 20°C.

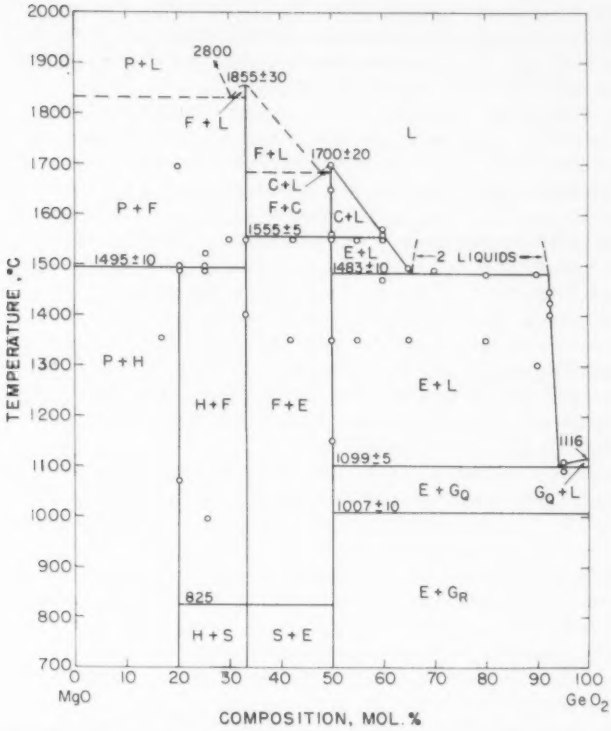

Fig. 1. Equilibrium diagram of the system MgO-GeO_2. The melting point of 2MgO.GeO_2 taken from Ringwood (1956). The inversion temperatures of 825°C and 1007°C taken from Dachille and Roy (1956) and Schafer and Roy (1956), respectively.

Symbol	Composition	Structure Type
C	MgO.GeO_2	probably Clinoenstatite
E	MgO.GeO_2	Enstatite
F	2MgO.GeO_2	Forsterite (Olivine)
G_Q	GeO_2	Quartz
G_R	GeO_2	Rutile
H	4MgO.GeO_2	—*
L	—	Liquid
P	MgO	Periclase (NaCl)
S	2MgO.GeO_2	Spinel

* Belongs to hexagonal system according to M. Rubenstein, (personal communication, 1958).

The region of two-liquid immiscibility occurs at 1483°C ± 10°C and extends from 8 to 34 mole percent MgO.

The range of immiscibility in the MgO-SiO_2 system is 1.2 to 40 mole percent MgO. Levin and Block (1957) estimated that the magnesia-rich liquid

of both systems would contain approximately the same mole percent of MgO. The 6 percent discrepancy between the corresponding magnesia systems cannot be adequately explained. A comparison of germania and silica systems containing other modifier oxides should be instructive.

The Compound: $4MgO.GeO_2$.—In preparing mixtures of the composition $4MgO.GeO_2$ by solid state reaction, complete combination could not be achieved. Heat treatment at about 900°C yielded a metastable assemblage consisting of MgO, GeO_2 (rutile form), $MgO.GeO_2$, and a trace of $2MgO.GeO_2$. With further heat treatment, $2MgO.GeO_2$ increased in amount whereas GeO_2 and $MgO.GeO_2$ disappeared. With prolonged treatment above 1150°C, the resulting product showed a new phase, $4MgO.GeO_2$, with a trace of uncombined MgO and $2MgO.GeO_2$. The presence of excess MgO suggested that the actual compound might have a lower proportion of MgO to GeO_2. Formulation of compositions with MgO to GeO_2 ratios of 7:2 and 3:1 did not eliminate the MgO and $2MgO.GeO_2$. In these mixtures, crystals of $2MgO.GeO_2$ were well developed and readily visible under the polarizing microscope, whereas with the 4:1 mixture, large 2:1 growth was never observed. The best growth of the new phase occurred in 4:1 mixtures.

Qualitative estimates based upon x-ray powder data and microscopic examination showed that compositions having less MgO than the 4:1 mixture, e.g., $7MgO.2GeO_2$ and $3MgO.GeO_2$, yielded the new phase, with a fair amount of $2MgO.GeO_2$, and a trace of MgO. Compositions richer in MgO than 4:1, e.g., $5MgO.GeO_2$, showed the new phase and MgO as major constituents, with trace amounts of uncombined $2MgO.GeO_2$. It was concluded, therefore, that the compound composition was $4MgO.GeO_2$. An attempt to obtain complete reaction by hydrothermal technique was unsuccessful.

At 1495 ± 10°C, $4MgO.GeO_2$ dissociates sluggishly to form $2MgO.GeO_2$ (forsterite form) and MgO.

The compound $4MgO.GeO_2$ is of particular interest since no corresponding 4:1 silicate is known. It is also of commercial importance as a basic phosphor composition. The composition $4MgO.GeO_2$:0.01Mn was patented by Williams (1948), and a number of papers have been published dealing with the properties of this phosphor and related compositions.

According to unpublished data of Martin Rubenstein (personal communication, May, 1958), $4MgO.GeO_2$ has a hexagonal unit cell with $a = 11.773$Å and $c = 14.448$Å. Crystals obtained in the present study had low birefringence (first order) with $N_p = 1.740$ and $N_g = 1.755$ ($\pm .003$). Those large enough to give interference figures were badly strained and showed a biaxial positive character with a small 2V. Although most of the peaks in the x-ray powder diffraction pattern could be indexed on the basis of a hexagonal unit cell, several peaks could not be assigned indices.

POLYMORPHISM

$2MgO.GeO_2$.—In the portion of the diagram between $4MgO.GeO_2$ and $2MgO.GeO_2$ the phases coexisting in equilibrium below 825°C are the 4:1 phase and the spinel form of $2MgO.GeO_2$. The latter was first reported by Goldschmidt (1931). It was of particular interest because it suggested that under proper conditions in the earth's mantle, the mineral forsterite (2MgO.

SiO_2) might be transformed from an olivine to a spinel structure. Both spinel and olivine forms of $2MgO.GeO_2$ were prepared hydrothermally by D. Roy and R. Roy (1954). Their reported values for the cell parameter and index of refraction of the spinel form are respectively a = 8.255Å and n = 1.76. F. Dachille and R. Roy (1956) studied the spinel-olivine transition in hydrothermal system and found that the transition takes place at 825°C at 10,000 psi.

The parameters of the olivine form as given by D. Roy and R. Roy are a = 4.915Å, b = 10.295Å and c = 6.020Å. Ringwood (1956) reported refractive indices, $\alpha = 1.708$, $\gamma = 1.765$ ($\pm.003$), for the olivine form. In the present study, using the oil immersion method and white light, the following optical properties were observed: $\alpha = 1.698$, $\beta = 1.717$, $\gamma = 1.765$ ($\pm.003$), and $+2V = \sim 65°$. Small tabular crystals showing high birefringence and parallel extinction were normally observed.

$MgO.GeO_2$.—Roth (1957) found the 1:1 compound to be isostructural with orthorhombic enstatite ($MgO.SiO_2$). He reported the following cell constants for the germanate: a = 18.661Å, b = 8.954Å, and c = 5.346Å.

In the present study the orthorhombic phase was shown to be stable up to about 1555°C. Crystals of this phase are characteristically lath-shaped, occasionally needle-shaped. Optical properties are: biaxial negative with 2V of about 70°, $\alpha = 1.741$, $\beta = 1.755$ and $\gamma = 1.759$ ($\pm.003$).

Samples quenched between 1555°C and the liquidus showed a monoclinic polymorph, the analog of clinoenstatite ($MgO.SiO_2$). Lath-shaped crystals are formed showing multiple twinning and an extinction angle of 20° to 22°, as in the silicate. The indices of refraction are: $\alpha' = 1.757$, $\gamma = 1.790$ ($\pm.003$).

The higher inversion temperature of orthorhombic $MgO.GeO_2$ (1555°C), as compared with that for orthorhombic $MgO.SiO_2$ (985°C) (Atlas, 1952) suggests that the substitution of Ge for Si in the silicate would raise its transition temperature.

Studies of the compound $MgO.SiO_2$ (Foster, 1951; Atlas, 1952) suggest that above the stability temperature of the orthorhombic form (enstatite), the polymorph protoenstatite is the stable phase. Upon standing or with annealing, this is known to invert to the monoclinic form (clinoenstatite). A protoenstatite phase was not observed in this work. However, it may exist in the germanate system, inverting to monoclinic $MgO.GeO_2$ on quenching. A detailed hydrothermal study might produce the phase, although several explatory experiments were unsuccessful. Its existence might be shown by using high-temperature x-ray diffraction methods as Foster (1951) has done with the silicate.

In this study, the monoclinic polymorph was obtained above 1555 ± 5°C and was found to invert sluggishly (7 days at 1375°C) to the orthorhombic form with heating below that temperature.

Table 1 gives the optical data and the unit cell constants for compounds in the system MgO-GeO_2. A list of d spacings and intensities for the 4:1, 2:1 and 1:1 phases obtained in this study is given in table 2.

CONCLUSIONS

In general the systems MgO-GeO_2 and MgO-SiO_2 are similar in that they have two analogous compounds and large regions of immiscibility. The ortho-

rhombic 2:1 germanate is isostructural with the 2:1 silicate and both melt congruently. The orthorhombic form of the 1:1 germanate is isostructural with enstatite; the monoclinic form of the 1:1 germanate is probably isostructural with clinoenstatite ($MgO.SiO_2$). The monoclinic form of the metagermanate inverts sluggishly to the enstatite form on heating below 1555 ± 5°C.

Of particular interest are the dissimilarities of the two systems. The analog of $4MgO.GeO_2$ is not known in the silicate system. In the latter system the temperature of two-liquid formation lies 18°C below the melting point of SiO_2, whereas in the MgO-GeO_2 system, the corresponding liquidus lies almost 370°C above the melting point of GeO_2. Within the limits of experimental determination $MgO.GeO_2$ melts congruently at 1700° ± 20°C, in contrast to $MgO.SiO_2$ which melts incongruently at the much lower temperature of 1557°C (Bowen and Andersen, 1914). Refractive indices of the magnesium germanates are higher than the indices of the corresponding silicates (by 0.06 to 0.13); likewise, the birefringence of the germanates is greater than that of the silicates (by a factor of two or more). A protoenstatite phase of the metagermanate, such as observed for the metasilicate, was not found in this work.

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TABLE 1
Some Properties of the Magnesium Germanates

Composition	Structure Type	Optical Properties	X-ray Parameters	Remarks
$4MgO.GeO_2$		$N_p = 1.740$ (±.003) $N_g = 1.755$ (±.003) uniaxial (+) or biaxial (+) with small 2V.	Hexagonal[1] a = 11.773 Å c = 14.448 Å	Sluggishly dissociates at 1495 ± 10°C to $2MgO.GeO_2$ (forsterite form) and MgO.
$2MgO.GeO_2$	Spinel	n = 1.76[2]	a = 8.255 Å[2]	Transforms[3] to forsterite (olivine) structure at 825°C
	Forsterite	+ 2V = ~65° $\alpha = 1.698$ (±.003) $\beta = 1.717$ (±.003) $\gamma = 1.765$ (±.003)	a = 4.915 Å[2] b = 10.295 Å c = 6.020 Å	Melts congruently at 1855 ± 30°C[4]
$MgO.GeO_2$	Enstatite	− 2V = ~70° $\alpha = 1.741$ (±.003) $\beta = 1.755$ (±.003) $\gamma = 1.759$ (±.003)	a = 18.661 Å[5] b = 8.954 Å c = 5.346 Å	Inverts above 1555 ± 5°C
	probably Clinoenstatite	$\alpha' = 1.757$ $\gamma = 1.790$ (±.003) Extinction angle 20-22°	a = 9.60 Å[6] b = 8.92 Å c = 5.16 Å $\beta = 100° 49'$	Melts congruently at 1700 ± 20°C. Sluggishly inverts to enstatite form below 1555°C.

[1] Rubenstein, M., personal communication, May, 1958.
[2] Roy, D. M., and Roy, R., 1954.
[3] Dachille, F., and Roy, R., 1956.
[4] Ringwood, A. E., 1956.
[5] Roth, R. S., 1957.
[6] R. S. Roth of the Natl. Bur. of Standards computed these values and found that all peaks in the powder pattern could be indexed on the basis of a c-centered lattice.

TABLE 2

Powder X-Ray[a] Data for the Magnesium Germanates

$4MgO.GeO_2$		$2MgO.GeO_2$ (Forsterite form)		$MgO.GeO_2$ (Enstatite Form)		$MgO.GeO_2$ (Clinoenstatite Form)	
d(Å)	RI	d(Å)	RI	d(Å)	RI	d(Å)	RI
5.92	8	5.15	21	6.46	5	6.46	16
5.11	17	4.42	38	4.70	18	4.74	35
4.82	33	3.91	100*	4.46	25	4.70	78
4.60	39	3.80	32	3.37	100	4.44	8
4.37	53	3.55	31	3.28	16	4.26	12
4.17	9	3.06	10	3.23	42	3.35	72
3.87	85	3.01	58	3.21	71	3.34	100*
3.74	35	2.96	3	2.99	100*	3.25	14
3.52	10	2.81	46	2.95	55	3.24	52
3.42	12	2.57	10	2.90	73	2.96	94
3.09	20	2.55	100*	2.76	20	2.90	100*
3.08	20	2.49	100*	2.57	35	2.78	33
3.02	4	2.45	10	2.56	43	2.58	48
2.97	25	2.39	22	2.53	31	2.53	100
2.89	18	2.37	37	2.46	6	2.47	5
2.80	17	2.29	20	2.37	5	2.44	11
2.79	21	2.28	21	2.31	7	2.43	28
2.75	3	2.22	61	2.23	8	2.37	9
2.654	19	2.08	16	2.11	4	2.26	5
2.648	17	1.99	22	2.05	6	2.23	100
2.57	18	1.96	17	2.02	8	2.12	20
2.52	100*	1.90	42	2.01	11	2.05	9
2.48	8	1.87	26	1.96	3	2.04	11
2.46	62	1.78	35	1.95	4	2.02	27
2.42	14	1.75	8	1.83	14	1.88	7
2.35	17	1.72	5	1.81	5	1.84	32
2.32	9	1.70	40	1.74	8	1.82	4
2.30	4	1.66	23	1.73	17	1.81	11
2.27	17	1.65	16	1.69	11	1.68	4
2.26	12	1.64	56	1.65	4	1.67	4
2.24	10	1.585	18	1.64	4	1.64	8
2.21	18	1.580	19	1.63	57	1.63	9
2.19	3	1.561	13	1.561	4	1.595	100
2.10	33[b]	1.539	16	1.558	5	1.582	7
2.09	27[b]	1.532	15	1.556	9	1.579	9
1.97	7	1.528	29	1.526	12	1.569	45
1.922	14	1.508	49	1.490	6	1.552	14
1.918	12	1.493	52	1.446	7	1.518	8
1.882	8	1.478	5	1.443	5	1.488	42
1.877	5	1.448	3	1.428	11	1.453	31
1.85	8	1.435	16	1.336	6	1.435	5
1.83	5	1.425	23			1.428	8
1.77	16	1.411	14			1.425	7
1.735	10	1.395	49			1.422	10
1.731	5	1.382	45			1.419	7
1.71	14	1.374	11			1.383	5
1.70	10	1.371	8			1.380	4
1.62	26	1.347	15			1.378	4
1.61	19	1.332	12			1.351	8
1.566	7	1.329	11			1.348	5
1.482	58					1.343	4
1.478	66					1.331	10

[a] Using Cu $K\alpha_1$ radiation, Ni filter.

[b] Intensity corrected for interferring MgO peak.

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PROPERTIES OF WATER. PART V. PRESSURE-VOLUME-TEMPERATURE RELATIONS OF WATER IN THE RANGE 400-1000 C AND 100-1400 BARS*

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ABSTRACT. New measurements of specific volume of water along 11 isotherms in the range 400-900 C were correlated and extrapolated to form a smooth table of specific volumes extending to 1000 C and 1400 bars.

INTRODUCTION

Prior to 1950 the specific volume of water had been measured in only a small part of this range, to 460 C and 350 bars (Keyes, Smith, and Gerry (1936)). The measurements of Kennedy (1950) extended to 1400 bars below 600 C and to lower pressures at higher temperatures, and were extrapolated to 2500 bars and 1000 C. Subsequently it was pointed out by Hilsenrath and others (1955, p. 437) that Kennedy's data were inconsistent at higher pressures and unreliable at lower pressures. The range 1-100 bars has since been remeasured by Kennedy (1957), using CuO to remove the hydrogen generated by reaction of water with the bomb wall. In the meantime new measurements of Kirillin, Rumiantsev, and Zubarev (1956) have appeared for temperatures to 650 C and to pressures of 500 or 900 bars.

In this paper we present the results of measurements made in 1956-1957, extending to about 1400 bars and 750 C, and to lower pressures at higher temperatures (1300 bars at 810 C, 700 bars at 865 C, and 400 bars at 905 C). The data are correlated and extrapolated to 1400 bars and 1000 C.

METHOD

The apparatus used in these measurements has been described in detail in previous papers of this series (Holser and Kennedy, 1958).

Most of the measurements were made on isotherms. The method is the same as that previously described, except that in many runs the measurements were carried down to about 40 bars, so that the rate of removal of water with change of pressure could be extrapolated to zero pressure. Such measurements were therefore independent of any other values except the specific volume of water at the temperature and pressure used (usually 200 bars, 200 C) in determining the volume of the bomb. Particularly in the lower part of the temperature range, the data were not sufficiently numerous or precise to make this extrapolation, and the previous low pressure measurements of Kennedy (1957) were used to establish the mass of water in the bomb at the lowest pressure on the isotherm.

* Publication no. 115, Institute of Geophysics, University of California, Los Angeles, California.

A total of 25 isotherms were run at the following temperatures: 420, 460, 500, 550, 620, 700, 750, 800, 810, 865, 905, and 950. A number of these covered the pressure range incompletely. The effect of hydrogen evolution became evident at 900 C, and necessitated the rejection of all the data for 950 C. At the latter temperature the presence of the CuO in the bomb was not sufficiently effective in reducing the hydrogen concentration during the length of time required for this type of run, although Kennedy's (1957) isometric runs at low pressures were apparently successful because they were in this region for only a brief time. Some other single measurements were also rejected on the basis of inconsistency or known operational errors.

In order to check the trend of isometric lines in the p-T plane, particularly for the purpose of extrapolation, other runs were made at approximately constant volumes of 4.71, 6.70, and 14.8 cc/g. A very long time would have been required to stabilize each temperature closely enough for measurements with the piston gauge. This would have increased the danger of errors due to slight leakage, or to creep of the bomb material near the upper limit of the runs. Therefore the pressures were read with the precision Heise Bourdon gauge.

REDUCTION AND CORRELATION OF DATA

The mass of water in the bomb at the low pressure end of an isothermal measurement was determined by the following method of extrapolation. The ratio $\Delta m/\Delta p$ for various pressure intervals from say, 500 bars, down to the lowest pressure of about 40 bars, was plotted against pressure. A smooth curve drawn through these points could then be extrapolated to find $\Delta m/\Delta p$ for the interval from zero pressure to the lowest measured pressure. These data could also be checked against the measurements of bomb volume in the following way. Assume that the ratio of differences is approximately equal to the derivative, dm/dp. Then near zero pressure the last bit of water in the bomb should be extracted under ideal gas conditions, for which

$$dm/dp = V/R'T \qquad (1)$$

where V is the measured volume of the bomb, and R' is the gas constant including the molecular weight of water. Strictly speaking, T is the absolute thermodynamic temperature. Preliminary calculations suggested that our data were probably not sufficiently precise to detect any differences (Keyes, 1949, p. 927) between the thermodynamic and International scales of temperatures, therefore International temperatures were used in all calculations and reduction of data. In other words, where the extrapolation of our measurements did not intersect $p = 0$ at the values of dm/dp calculated from equation (1) and the International temperature, the difference could usually be attributed to errors of measurement. Otherwise the difference might have been attributed to the fact that the extrapolation depended on a thermodynamic temperature while equation (1) was calculated with an International temperature. Most of the differences were small and showed no general trend.

A final mass, determined either in the above fashion or by the use of Kennedy's (1957) data, was the basis for the calculation of specific volumes at each higher measured pressure.

Each isotherm was smoothed by the method of item differences described previously. Inasmuch as the function $z = pv/RT$ varied less sharply with pressure than did the specific volume, the function $\Delta z/\Delta p$ was plotted against p. This turned out to be a very satisfactory method of smoothing small irregularities in the isotherm measurements, except below 400 bars and 500 C, where $\Delta z/\Delta p$ varied sharply.

Isotherms in the unmeasured region above 750 C were determined by extrapolating the trend of isometrics in the p-T plane. In order to determine the trend of a given isometric accurately, it was necessary to make a precise interpolation at that specific volume on each isotherm. Inasmuch as a precise curve of $\Delta z/\Delta p$ (derived directly from the data) was already available for each isotherm, it was used in the following way as an aid to interpolation. Assuming that the variation of z with p is nearly linear, then near z_o, p_o

$$Z = Zo + \frac{\Delta z}{\Delta p} \quad (p - p_o) \tag{2}$$

and also

$$Z = \frac{pv}{RT} = \frac{p_o v}{RT} + \frac{(p - p_o)\, v}{RT}$$

therefore

$$(p - p_o) = \frac{z_o - p_o v/RT}{v/RT - \Delta z/\Delta p} \tag{3}$$

Using this equation one can precisely calculate the pressure p for a given v, using known nearby values of p_o, z_o, and $\Delta z/\Delta p$. A more precise calculation may be made by assuming a quadratic form in place of equation (2), and measuring the slope of the $\Delta z/\Delta p$ vs. p curve near z_o, p_o. A solution for $(p - p_o)$ in this case requires a series expansion, of which the first term is given by equation (3) above, but even the second term is not significant for most interpolations.

Isometrics derived in this fashion seem nearly straight on a large scale plot, but differencing to get $\Delta p/\Delta T$ confirms a slight concavity towards the T axis. Plots of this function against temperature were extrapolated and reintegrated to obtain values of pressure at temperatures above the range of measurement. The combination of measurements along isotherms, and higher isotherms derived by extrapolation along isometrics, gave a set of isothermal measurements at temperatures to 1000 C. Cross-smoothing at high temperatures was then done in an analogous fashion, using a plot of $\Delta z/\Delta T$ vs. T. This same plot could also be used to interpolate temperatures between the measured isotherms. At temperatures below 700 C this method could not be used because $\Delta z/\Delta T$ varied too sharply over the temperature intervals measured. Smoothing and interpolation at these low temperatures was done on a large scale plot of z vs. T.

The final results are tabulated in terms of specific volume in table 1. These final values are most easily compared with the measurements of the

original isothermal runs in terms of z[1]. For most runs the standard deviation is 0.0005 – 0.0020 in z. Both runs at 420 C below 500 bars, and one of the runs at 460 C, had standard deviations of 0.0025 – 0.0030 in z. In view of the good agreement between Keyes and Kirillin at 420 C, their measurements were used for table 1 below 500 bars in that region. At nearly all temperatures each of our runs showed greater internal consistency than the deviations from the table, indicating that the factors varying between runs (bomb volume and temperature) are probably the major source of uncertainty in table 1. Above 620 C the deviations of the measurements from table 1 are in part a reflection of the smoothing among isotherms, but at lower temperatures the isotherms were not sufficiently close for such smoothing to contribute very much to the deviations.

COMPARISON WITH THE RESULTS OF OTHER INVESTIGATORS

This series of measurements overlaps those of Keyes, Smith, and Gerry (1936) only at 420 and 460 C, up to 360 bars. In view of the low precision of some of our runs at these temperatures, a special series of 4 single measurements were made at 460 C and 350 bars, to determine whether there was any fundamental disagreement with the data of Keyes and the equivalent data of Kirillin. The average difference between these experiments and Keyes-Kirillin was 0.0005 in z, which cannot be considered significant.

The 20 isotherms of Kirillin, Rumiantsev, and Zubarev (1956) deviate from table 1 not more than $\pm$ 0.002 in z, except as shown in table 2. Thus the greatest discrepancy between Kirillin and ourselves is at the high temperature end of his series, above 600 C. His data at 650 C are internally inconsistent, and therefore our measurements are probably to be preferred in this range until an independent check has been made.

The earlier table by Kennedy (1950) deviates considerably from table 1. At 1400 bars the difference in z decreases with temperature to a minimum of –0.006 at 500-550 C, then increases through zero at 630 C to +0.020 at 800 C and +0.025 at 1000 C. Below 1000 bars the differences are substantially less: at 500 bars the minimum is –0.002 at 500 C, zero at 560 C, a maximum of +0.004 at 750 C, and drops to +0.001 at 1000 C. Below 300 bars the early results are very erratic and mostly low.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research under contract Nonr 233(27). A large number of persons in this laboratory contributed to this project at various stages with assistance in calculations and experiments. Thanks are particularly owing to Lester Emerine who constructed equipment and kept it in good repair. G. J. F. MacDonald has critically read the manuscript.

[1] Available as document no. 5803, American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE 1

Specific Volume of Water in cc/g

Pressure Bars	420	440	460	480	500	520	540	560	580	600	620	640	660	680	700
150	16.86	17.95	18.97	19.92	20.82	21.68	22.50	23.31	24.10	24.88	25.64	26.40	27.14	27.87	28.59
200	11.203	12.232	13.161	14.008	14.783	15.52	16.21	16.88	17.52	18.16	18.77	19.38	19.97	20.55	21.12
250	7.579	8.675	9.604	10.414	11.141	11.803	12.425	13.015	13.581	14.125	14.655	15.17	15.67	16.16	16.64
300	4.917	6.221	7.178	7.991	8.703	9.322	9.899	10.437	10.947	11.435	11.907	12.365	12.809	13.238	13.653
350	3.084	4.397	5.419	6.247	6.953	7.545	8.091	8.593	9.066	9.516	9.947	10.364	10.767	11.152	11.526
400	2.368	3.215	4.153	4.953	5.639	6.217	6.726	7.213	7.659	8.081	8.482	8.869	9.239	9.594	9.937
450	2.089	2.564	3.278	4.005	4.660	5.210	5.703	6.154	6.575	6.974	7.352	7.711	8.055	8.386	8.704
500	1.942	2.271	2.750	3.337	3.906	4.426	4.896	5.326	5.727	6.102	6.457	6.793	7.116	7.427	7.726
600	1.774	1.975	2.239	2.573	2.963	3.365	3.758	4.133	4.489	4.823	5.141	5.443	5.731	6.007	6.272
700	1.675	1.815	1.995	2.217	2.476	2.764	3.068	3.372	3.671	3.962	4.244	4.515	4.774	5.020	5.257
800	1.607	1.716	1.850	2.010	2.195	2.405	2.636	2.880	3.128	3.375	3.620	3.857	4.085	4.305	4.518
900	1.554	1.645	1.750	1.874	2.018	2.179	2.358	2.553	2.757	2.965	3.174	3.380	3.580	3.775	3.964
1000	1.512	1.589	1.677	1.779	1.895	2.026	2.170	2.327	2.494	2.669	2.848	3.026	3.201	3.373	3.541
1100	1.477	1.544	1.619	1.705	1.802	1.910	2.030	2.162	2.303	2.451	2.604	2.758	2.911	3.063	3.213
1200	1.447	1.506	1.572	1.646	1.729	1.822	1.925	2.037	2.158	2.285	2.417	2.550	2.684	2.819	2.953
1300	1.421	1.475	1.533	1.598	1.671	1.752	1.840	1.938	2.043	2.153	2.268	2.385	2.503	2.623	2.744
1400	1.398	1.448	1.501	1.559	1.624	1.695	1.772	1.858	1.949	2.047	2.148	2.251	2.356	2.464	2.574

TABLE 1 (Continued)

Pressure Bars	720	740	760	780	800	820	840	860	880	900	920	940	960	980	1000
150	29.30	30.00	30.68	31.36	32.04	32.72	33.40	34.07	34.74	35.41	36.08	36.74	37.41	38.07	38.74
200	21.67	22.22	22.75	23.28	23.81	24.33	24.85	25.37	25.89	26.40	26.91	27.42	27.93	28.44	28.96
250	17.10	17.55	18.00	18.44	18.87	19.30	19.73	20.16	20.58	21.00	21.42	21.84	22.26	22.68	23.09
300	14.056	14.450	14.837	15.22	15.59	15.96	16.33	16.69	17.05	17.41	17.76	18.12	18.48	18.83	19.19
350	11.888	12.240	12.584	12.919	13.249	13.575	13.897	14.216	14.533	14.848	15.16	15.47	15.78	16.10	16.41
400	10.267	10.587	10.899	11.202	11.499	11.793	12.082	12.367	12.651	12.933	13.212	13.490	13.769	14.048	14.327
450	9.010	9.306	9.592	9.871	10.143	10.411	10.674	10.935	11.193	11.448	11.702	11.954	12.206	12.458	12.710
500	8.011	8.286	8.552	8.810	9.061	9.309	9.552	9.793	10.031	10.266	10.498	10.729	10.960	11.191	11.421
600	6.525	6.769	7.004	7.231	7.452	7.669	7.881	8.091	8.299	8.502	8.704	8.903	9.102	9.301	9.497
700	5.484	5.702	5.912	6.117	6.316	6.509	6.700	6.887	7.073	7.254	7.434	7.611	7.786	7.961	8.134
800	4.722	5.920	5.111	5.296	5.476	5.652	5.825	5.996	6.163	6.328	6.490	6.650	6.809	6.965	7.120
900	4.149	4.328	4.501	4.670	4.835	4.997	5.156	5.312	5.465	5.616	5.765	5.911	6.055	6.197	6.338
1000	3.707	3.870	4.028	4.183	4.334	4.483	4.629	4.773	4.914	5.053	5.190	5.325	5.457	5.588	5.717
1100	3.362	3.509	3.654	3.796	3.935	4.072	4.207	4.340	4.471	4.599	4.726	4.851	4.974	5.094	5.213
1200	3.087	3.220	3.352	3.482	3.611	3.738	3.863	3.986	4.107	4.227	4.345	4.461	4.575	4.688	4.798
1300	2.865	2.986	3.107	3.227	3.345	3.462	3.578	3.692	3.805	3.916	4.026	4.135	4.242	4.347	4.450
1400	2.684	2.795	2.905	3.016	3.125	3.233	3.340	3.446	3.550	3.654	3.757	3.858	3.959	4.058	4.155

TABLE 2

Comparison with Data of Kirillin, Rumiantsev, and Zubarev (1956)

All other differences less than ±0.002 in z

Kirillin isotherm deg C	Pressure range bars	Difference of compressibility factor Kirillin less table 1
410.00	300	+0.004
431.34	450-500	+0.003 to 0.004
437.00	450	+0.004
461.65	350-450	−0.003 to 0.006
500.00	450-500	−0.003
500.27	450-600	−0.003
501.31	350-500	−0.003
551.45	300	−0.003
620.00	200-300	−0.004 to 0.005
650.00	150	+0.004
650.00	250-500	−0.004 to 0.008

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REVIEWS

Principles of Geodynamics; by ADRIAN E. SCHEIDEGGER. P. xi, 280; 86 figs. Berlin, 1958 (Springer-Verlag, DM 49.60).—Geodynamics is nowhere defined in this book. If we take the Table of Contents as indicating the range of subject matter which Scheidegger considers as geodynamics, then geodynamics is concerned with the rotation of the earth, the origin of continents and oceans, mountain building, the dynamics of faulting and folding, meteor craters, domes, volcanism, post glacial uplift, and boudinage. The inclusion of the last subject among such large scale and even cosmic events is somewhat surprising. This is not the last surpise a geologist or even a geophysicist reading Scheidegger's book will encounter.

Since geodynamics is concerned with the origin of the earth's surface features it is not surprising to find that Scheidegger includes a review of geologic data regarding the earth. Indeed Scheidegger devotes 29 of his 290 pages to the data with which geodynamics is presumably concerned. The content of the first 29 pages is certain to amaze many. The principal emphasis is on a description of the assumed arcuate structure of mountain belts. Aside from arcuate structures Scheidegger does consider a few common geologic concepts. On page 12 the geosyncline is referred to as a down-buckled trough, while on page 20, a geosyncline is alternatively considered as a break with substantial horizontal and minor vertical movements. No mention is made of the rocks of the geosyncline. A page is devoted to the description of folds, and we are told that strata in mountain ranges have been contorted to a fabulous extent. The authority for this last statement is none other than Scheidegger himself, who refers the reader to his article in the Handbuch der Physik. On examining this article, one does not find anything in the way of references to the original geologic work. A confused reader of the first chapter, and there are likely to be many, has nothing in the way of guidance to articles or books that will explain geology somewhat more clearly than Scheidegger has been able to do.

The physics that Scheidegger uses is often as confusing and surprising as is his geology. He interprets the damping of the Chandler wobble of the earth in terms of a Kelvin spring-dashpot model. If the earth behaves as a Kelvin body with the constants derived from the damping of the Chandler motion, then we would have no more fear from earthquakes as was pointed out many years ago by Jeffreys. However, Scheidegger is not alone in using linear rheologic models to explain the non-elastic behavior of the earth. What Scheidegger does not realize is that there is no experimental nor observational justification for the continued use of these models.

Much of the book is concerned with a review of theories on the origin of the earth's surface features. This part is done in a reportorial style. The arguments are reproduced more or less as they were originally presented. Scheidegger adds critical comments to many of the theories. These comments are distinguished by the fact that the criticisms are invariably based on supposed objections from physics or geophysics rather than on geologic data. This section leaves one with the impression that it was written by a physicist who is horrified by the complexity of geodynamics.

More disturbing than the contents of the book are the ideas that Scheidegger expresses in the Preface. Scheidegger's view of geodynamics is

that of a static science. Scheidegger claims that the basic theories have been conceived in principle during the 19th century and not much has been added. Indeed, geodynamics is thought by him to be 2000 years behind physics. The aparent complexity of the subject leads Scheidegger to the belief that not much new will be done in geodynamics for many, many years. Nothing could be further from the truth. The recent developments in a wide range of subjects make geodynamics one of the most exciting fields of inquiry in science today. The study of the rotation of the earth is a typical example. The development of the moon camera and of the ceasium clock have revolutionized time-keeping. We will now be able to follow in far greater detail the motions of the earth. Experimental geodynamics is in the state of healthy infancy. Only in the last few years has the study of material at high pressures and temperatures, equivalent to conditions existing within the earth, reached any degree of sophistication.

It is easy to see how Scheidegger reached his pessimistic view of geodynamics. Scheidegger restricts his study to the theories of geodynamics. Much of the work in this field does read like bad philosophy. Continued work in the area of the classical theories of mountains, continents, etc. can rapidly lead to confusion and pessimism if not tempered by a critical evaluation of the relevant data. Fortunately, the lack of geological understanding revealed in this book makes it unlikely that many workers will be discouraged from continuing or beginning the study of geodynamics.

GORDON J. F. MAC DONALD

Physical Geology; by L. Don Leet and Sheldon Judson. P. vi, 502; 412 figs., 37 tables. New York, 1958 (Prentice-Hall, Inc., $7.50).—This second edition of Leet and Judson's *Physical Geology* is a reorganized, revised, and almost new book. Three new chapters are Minerals, Geologic Time, and Lakes and Swamps; other separate chapters are created from previous combinations. In some chapters every sentence is rewritten with drastic reduction; in others only introductory paragraphs are new with large sections bodily reprinted with hardly a change. The chapter on The Earth's Age and Place in the Universe is eliminated. Many fine photographs still adorn the book, with a goodly share of those being Vittorio Sella's, the famous mountain photographer. Colored end papers of three geologic sections across Canada, across United States, and across Mexico are an innovation.

The book is still written for the moderately intelligent student with a modern background in elementary chemistry and physics. Chapter 2 on Matter and Energy, a real stumbling block in the first edition, now is so simplified and understandable that all except the uninterested will find little difficulty with it. The lecturer, however, still needs to justify such information for his students. Explanation later comes in part in the following chapter on Minerals and on the relationship between their chemical and physical properties and their internal atomic structure. Appendix C now is in part an 8-page Common Minerals identification chart.

In the chapter on Geologic Time, the Geologic Column and Time Table are especially modern with the avoidance of the out-dated terms Tertiary and

Quaternary. In later chapters, the concepts of peneplanation and of cycles of erosion unfortunately still are considered worthy of attention. The excellent chapter on Glaciation is prefaced by an introduction to glaciology. The treatment of arid and semi-arid region landscapes is far too scanty for its importance and still needs amplification. Lakes and Swamps offers unexpectedly interesting new material. The latter part of the book on Rock-Deformation and Mountain-Building, Metamorphism, Earthquakes, and The Earth's Interior involves the "deepest thinking" type of geology and is well done, with latest ideas and present status of controversial subjects offered as well balanced summaries of opposing theories. The Glossary of 706 items (108 more than in the first edition) stands independently as a dictionary of geologic terms.

This top-notch book should bring to geology, as a young science, the high standards of endeavor and respect that chemistry and physics now enjoy. This edition, so tremendously improved over the first, certainly deserves a second serious consideration as a textbook by all teachers of geology.

SIDNEY E. WHITE

Old Stone Age; by STEVAN CELEBONOVIC with a commentary by GEOFFREY GRIGSON. P. 92; 2 figs., 72 photographs in 64 pls. Publication of Nature and Art: a Series. London, 1957 (Phoenix House, $10.00).—This volume combines a masterpiece of photography of Paleolithic artifacts and art by Célébonovic with Grigson's popular introduction to the study of man of the Old Stone Age. Both authors limit their scope of interest to European cultures with a particular emphasis upon the Upper Paleolithic period. Thus out of the total of 72 photographs only 4 deal with the Lower Paleolithic.

The artistic pictures should prove useful to beginning students of European archeology and of history of art. The photographs and the "immaginative text by Geoffrey Grigson in which the poet-scientist endeavors to guess what passed in the minds of these stone age men," however, seem to be directed primarily toward a popular reader who seeks in reading more entertainment than instruction. Thus the lyric and philosophical introduction by Célébonovic discloses a strange evolutionist theme which relates magic with art. Also, the text (22 pages) by Grigson presents the reader with a mixture of scientific facts, philosophic reasoning, and pure speculations as to the beginning and development of art, relationship between art and nature, and attitudes and mental processes of the Stone Age artists. Thus the value of otherwise adequately formulated outline of the European Stone Age cultures is dimmed by unnecessary guesses and theories which make it difficult for a beginning student to separate poetry from scientific facts.

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